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RATE STUDIES OF THE CATALYTIC REACTION
OF H_2S AND SO_2

by



BRYON LEROY KARREN

A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled RATE STUDIES OF THE CATALYTIC REACTION OF H_2S AND SO_2 submitted by BRYON LEROY KARREN in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

An experimental program to investigate the kinetics of the reaction between H_2S and SO_2 was carried out. A commercial bauxite sulphur conversion catalyst was used. The kinetic measurements were made in a flow recycle reactor with a differential catalyst bed. The volumetric feed rate and feed and product composition enabled the calculation of isothermal rates of reaction at various conditions.

A gas chromatograph analysis was employed to measure the feed and product compositions. The gas chromatograph areas were measured by an on-line IBM 1800 computer. Prior to implementing the on-line area measurement a thorough investigation of the gas chromatograph monitoring program package was carried out to evaluate its capabilities for this specific analysis and other general analyses.

The rate measurements were made at one temperature only, 515°K ($\pm 1^\circ$), and at a total reaction pressure of approximately 830 mm Hg. Throughout the course of the experimental program the ratio of the two reactants was varied extensively, as well as the feed to catalyst ratio. A number of runs were made to observe the effect of the presence of water, one of the products, in the feed. The conversion of H_2S was varied between 9% and 94% while the H_2S rate of reaction varied from 0.01 to 0.23 (gm.-moles/hour/gm. catalyst).

To allow the analysis by the gas chromatograph the product stream was passed through a condenser to remove sulphur. A series of experiments performed late in this study showed that an appreciable amount of H_2S - SO_2 conversion occurred in this condenser. The reaction appeared to be catalysed by the condensed sulphur. This meant that the product compositions obtained were not those of the reactor. Since

it was not possible to separate the contribution of the conversion due to the catalyst and that due to the sulphur condenser, no attempt was made to correlate the obtained rate data to kinetic models.

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I. INTRODUCTION

1.1 Background

The primary goal of this study was data acquisition over a wide range of variables to provide an improvement to the rate correlations previously obtained for the Claus reaction (34,11). Most of the previous data were not at high enough conversions to be influenced by the reverse reaction.

In order to streamline the data acquisition a program designed to eventually result in a completely on-line reactor system was undertaken. As pointed out by McGregor (34), the first and most important requirement to allow on-line operation was a suitable on-line analysis. A gas chromatograph monitoring program that was originally supplied by IBM (26), and had subsequently been modified by Coxhead (9), was further modified by the Chemical and Petroleum Engineering DACS Centre staff. The principle modifications by the last group was the inclusion of a variable scan rate, and the change-over to operation in a multiprogramming mode (MPX). These modifications appeared to have rectified all of the previous problems and a decision was made to use this system rather than a modified system used on this reactor previously by Liu (31).

1.2 Claus Reaction

The reaction of H_2S and SO_2 has been utilized for sulphur production for more than a century. The occurrence of H_2S in many natural gas fields made the process even more common, as a means to produce a useful byproduct in the process of preparing the natural gas for market.

Interest in the reaction mechanism and a suitable equation to predict reaction rates over a wide range of conditions was motivated by

the need to reduce sulphur losses and to operate the reactors as efficiently as possible.

1.3 Equipment

The equipment used in this study was originally designed and operated by McGregor (34). A continuous flow recycle reactor with a differential bed was employed to allow the acquisition of isothermal data. By operating at a sufficiently high recycle to feed ratio it was possible to apply a continuous stirred tank reactor material balance.

McGregor used the equipment to study the H_2S and SO_2 reaction with a commercial bauxite catalyst over a conversion range from 5 to 20 percent. Statistical treatment of the data (11) indicated that the data was not influenced by any contribution of the reverse reaction.

Liu (31) modified the equipment slightly to study the COS and SO_2 system. This system was of interest due to the large contribution of sulphur losses to COS in actual plants (30). He also utilized the apparatus to study the Claus reaction and the COS reaction over other catalysts that were being tried in the sulphur industry.

1.4 Objectives and Results

By employing larger catalyst charges and lower feed rates it was possible to extend the data obtained by McGregor (34). A further variation in reaction conditions was also obtained by the addition of H_2O to the feed.

Procuring of usable data in this research program was hindered by problems in the analytical procedure. It was discovered that the reaction was catalysed by the condensation of sulphur from the product stream. It had previously been observed that liquid water was an active

catalyst for the reaction (34). McGregor had taken precautions to eliminate condensing of water from the product stream. However, the analogous error introduced by sulphur condensation was not recognized by him. Unfortunately, the removal of sulphur was necessary to allow the gas chromatograph analysis. Therefore, no simple solution was available to correct the situation.

1.5 Evaluation of the Gas Chromatograph Monitoring Program

As stated previously, one objective of the project was to further develop the computer data acquisition capabilities of the equipment. The main barrier to a complete on-line system had been the difficulty in performing suitable on-line analyses (34,31). A computer program package was evaluated in this project to ascertain its capabilities. The testing of these programs covered some features not required for the gas chromatograph analysis of this project, but of general interest in the field of gas chromatography and computers. Some recommendations were made that would further improve the package as a result of this study.

II. LITERATURE SURVEY

2.1 Studies of the Claus Reaction

Gamson and Elkins (16) studied the Claus reaction with an integral reactor packed with Porocel catalyst. They measured conversions of one feed gas at varied temperatures and space velocities. They measured conversions that were 1 to 3 percent higher than their equilibrium calculations indicated were thermodynamically feasible. Their cited temperatures were likely "point" temperatures since their integral reactor would probably not operate isothermally for this reaction. No attempt was made to obtain rate data from their results.

Murthy and Rao (37) studied the Claus reaction over metallic sulphide catalysts. They employed a batch recycle reactor operated at 25°C. The deposition of sulphur on their catalyst lead to a continuous unsteady state situation with regard to catalyst surface area.

Taylor and Wesley (46) obtained a rate equation for the reaction on pyrex glass. They concluded that no homogeneous reaction occurred since they were able to demonstrate that the reaction rate was proportional to the catalyst surface area.

Udintseva and Chufarov (49) found glass, aluminum, and aluminum oxide to be good catalysts for the Claus reaction. Iron and iron oxide were found to catalyse this reaction only slightly. During the course of their work they verified that no homogeneous reaction occurred between 250°C and 350°C.

Hammar (22) studied the Claus and other related reactions on a cobalt-molybdenum-alumina catalyst. McGregor (34) pointed out possible errors resulting from Hammar's method of chemical analysis which may

prejudice Hammar's results. Hammar observed the retardation of the rate of reaction by the products and also concluded that the reaction rate was dependent on the external surface area of the catalyst.

Cormode (8) obtained kinetic data using a recycle flow reactor with a commercial bauxite catalyst. His method of chemical analysis involved an absorption train and wet chemical techniques.

McGregor (34) employed a recycle flow reactor to measure isothermal reaction rates. He performed experiments with total conversions of less than 20 percent at temperatures between 208°C and 287°C. The H_2S to SO_2 ratio was varied as well as the two reactant concentrations. The experimental program included tests for homogeneous reaction, external mass transfer controlling step, and constant catalytic activity. The reaction rate was found to be proportional to the external surface area of the catalyst and to exhibit an inverse relation to the H_2O concentration. A subsequent statistical treatment of his data (11) indicated that no appreciable reverse reaction had occurred in his experiments.

Wiewiorowski (51) did a qualitative study of the H_2S - SO_2 reaction in a liquid sulphur medium. An ethylenediamine catalyst was employed at concentrations ranging from 1 to 5000 ppm with 50 ppm cited as the preferred level. The reaction temperature was limited to temperatures between 120°C and 160°C by the properties of liquid sulphur. No mention was made of a possible reaction without a catalyst present.

2.2 Gas Chromatographic Analysis of Sulphur Gases

Hodges and Matson (25) investigated various solid-liquid and solid stationary phases for the separation of CO_2 , H_2S , SO_2 , COS and CS_2 . They were not able to obtain a complete analysis with any of the

solid-liquid combinations that they tried. A partial analysis was possible employing a two-temperature technique. Triton X-305 on Diatoport S at 25°C and 75°C separated air, H_2S , CS_2 and SO_2 . They also were able to analyse air, CO_2 , COS, H_2S and SO_2 using an isothermal silica gel column. However, the first 4 components eluted in the first two minutes and the SO_2 peak lasted for 3-1/2 minutes. If H_2O were present it had to be precut from the analysis or allowed to elute between injections. They were only able to get acceptable results using Davison 08, 80-100 mesh silica gel.

Jackson and Perry (28) discussed the analysis of sulphur plant streams with respect to sampling, separation, and interfacing to process control devices. Their separation scheme required a precut column of Dow Corning to remove H_2O , CS_2 and S. They reported two different columns that provided acceptable results: Dow Corning, and Porapak R. Large amounts of COS caused the COS and SO_2 to be fused on the first column and the second produced a broad SO_2 peak.

Obermiller and Charlier (38,39) employed a dual column, two temperature, split flow technique to analyse N_2 , O_2 , Ar, CO, CO_2 , H_2S , H_2O , COS and SO_2 . Both columns were packed with Porapak Q; their operating temperatures were -65°C and 75°C. The He carrier gas contained 100 ppm SO_2 to maintain the Porapak Q in a conditioned state. If H_2O was present to a significant extent, an overlap with H_2S appeared to be possible from the chromatograms they showed.

Leveque (30) described a sampling and separation scheme employed to measure sulphur plant efficiencies. A two column isothermal analysis was achieved using 3 flow modes; 1) two columns in series, 2) first column alone, and 3) second column alone. The first column was actually

a composite of 20 percent Triton X-305 on Chromosorb W followed by a short section of Porapak Q. The second column was Porapak Q. Water was present but no mention was made regarding its elution time or peak shape.

Thornsberry (47) investigated the use of Deactigel, a deactivated silica gel, as a replacement for silica gel. He found that silica gel caused excessive SO_2 tailing and was not consistent in characteristics from batch to batch. Deactigel was reported to eliminate these problems. He also reported that Porapak Q-S provided a separation of all of the gases except CS_2 . CS_2 was strongly held by the column and eluted as an extremely broad non-quantitative peak.

Patrik, Schrodtt, and Kermode (40) investigated various liquid phases on Chromosorb 104 for the separation of air and SO_2 . They had previously tried a silica gel analysis without satisfactory results.

Liu (31) employed a dual column arrangement to separate N_2 , CO_2 , COS and SO_2 . The columns were both silica gel but of varying lengths. The SO_2 only passed through the first short column to avoid tailing, while the N_2 , CO_2 and COS passed through both columns to provide an adequate separation. If H_2O were present it was backflushed to the vent from the first column after the elution of SO_2 .

McGregor (34) used a dual column arrangement to separate N_2 , H_2S and SO_2 in the presence of H_2O . A column of propylene glycol on Chromosorb G was followed by a short silica gel column. The analysis required 1 mode switch to backflush H_2O to the vent from the first column while the SO_2 was eluting from the second.

2.3 Gas Chromatograph-Computer Systems

2.3.1 IBM Computers

IBM issued a gas chromatograph monitoring system for their IBM 1800 computer (26). This system was hindered by the lack of a variable scan rate. Most of the subsequent monitoring programs for IBM computers were modified forms of this original one.

McCullough (33) discussed the general hardware and software requirements for monitoring a gas chromatograph. His analysis did not consider a variable scan rate approach.

Briggs (6) reviewed the operation of a system on an IBM 1800 computer at the Monsanto Company. The package appeared to be an unmodified version of the original programs. The system handled as many as 20 chromatographs and 3 mass spectrometers simultaneously. The chromatographs were scanned at 4 points per second.

Tivin (48) described a modified version implemented at Proctor and Gamble. The package operated at a constant scan rate of 6 points per second. A multiple reference peak feature had been implemented to aid in peak identification during complex analyses. A dual input approach was taken to obtain maximum resolution for small and large peaks.

Raymond, Lawrey, and Mayer (41) discussed a modified package in use at Sun Oil. They incorporated a variable scan rate from 1 to 12 points per second. It handled as many as 16 chromatographs simultaneously.

An on-line system for an IBM 1130 was described by Craven, Everett, and Rubel (10). This system handled 30 gas chromatographs simultaneously with a maximum multiplexer rate of 240 points per second. The system featured variable scan, multiple reference peaks, and a programmable gain amplifier.

A partial on-line system was reviewed by Gladney, Dowden, and Swalen (19) of the IBM Corporation. Data was gathered in real-time mode

and fit iteratively off-line. A least squares technique was employed to fit the data to a convoluted Gaussian shape. The fitting required 45 seconds overhead time and approximately 6 to 8 seconds per peak. The package was designed to handle peaks from gas-liquid chromatography.

An updated program package was released by IBM (27). It included variable scan rate, programmable gain attenuation, and off-line shape fitting peak resolution. Additional scan statures and additional filtering were added as well. This package is available for either TSX or MPX operating systems.

2.3.2 Varian Aerograph

Gill (18) discussed monitoring systems in general with respect to types of systems, costs, and future improvements. He considered 5 types of systems: 1) off-line, 2) hybrid, 3) time shared, 4) multi-channel dedicated, and 5) dedicated.

Baumann, Herlicska, and Brown (4), of Varian, described a system which gathered data in real-time. The data were taken at a constant scan rate and first derivatives were used for peak detection. In order to pick peaks of different shapes a variable scan was simulated by a "moving average" technique with a variable number of points. As the peak widths increased, more points were averaged together to form one point for the first derivative calculation.

Baumann, Brown, and Mitchell (5) reviewed the same system with respect to fused peak separation, interfacing details, job definition, and accuracy. To make job definitions easier for non-computer orientated personnel a special hardware job definition facility was implemented.

2.3.3 Electronic Associates Inc.

An EAI monitoring package was described by Hancock and Lichenstein (23). This package made use of second derivatives for peak detection. Fused peaks were separated by a bi-Gaussian approximation and shoulders were treated with a transformation technique.

Wilson and Price (52) discussed the implementation of a system on an EAI 640 computer at the Celanese Corporation. The same system was installed at two locations, one for quality control, and one for research applications. Twenty instruments were monitored simultaneously in a dedicated mode. The improved accuracy obtained by this system was discussed in some detail.

2.3.4 Others

Burke and Thurman (7) tested a system on a Hewett Packard 2115 A computer for the purposes of thermodynamic measurements. They were interested mainly in evaluating available hardware to determine the feasibility of such an application.

Watson (50) of Data Associates Incorporated discussed the interfacing of gas chromatographs to time shared computers and outlined desirable software features. He cited the necessity of a variable sampling rate and a programmable gain amplifier.

Stevens and Villalobos (45) described a system using a PDP 8/I computer. The mini-computer was dedicated to the chromatographs and had the capability of passing information either to a larger computer, or to conventional process control instrumentation. This system incorporated programmable gain amplification, but used a constant scan rate.

Mears (35,36) reviewed a system implemented at Mobil Oil. A dedicated mini-computer was linked to a larger computer. It was a

complete real-time system utilizing the first derivative for peak detection. Every instrument was polled 10 times per second.

Lyons (32) discussed the economics of implementing a computer system. The time savings for various complexities of analysis were discussed. He cited 2 years as a payoff time for a £ 41,550 system.

Frazer, Kray, Bertoglio (15) described a highly interactive system that allowed the chromatograph operator to make decisions about peak separation and baseline positioning. The operator communicated with the computer system through a graphical display terminal.

III. EQUIPMENT AND EXPERIMENTAL PROCEDURE

3.1 Introduction

The continuous flow recycle reactor and supporting equipment used in this study were essentially those used by McGregor (34). Some minor changes were made by Liu (31) to allow larger catalyst charges and improved operation of the sulphur condenser. Minor changes were made during the course of this work to improve the stability of the feed system and to increase the on-line data acquisition facilities.

3.2 Reactor and Recycle Loop

The reactor assembly, as modified by Liu (31), was used for this work in order to allow larger catalyst charges to be used. Figure 3.1 shows a detailed diagram of the catalyst holder. The fabrication was of 316 stainless steel. A 200 mesh stainless steel screen was employed to hold the catalyst charge. The recycled gases were pumped downwards through the catalyst bed.

A sliding vane compressor was employed to recycle the gases. The compressor body was constructed of 316 stainless steel and the vanes were constructed of graphite. This allowed the compressor to operate without grease or oil at temperatures up to 800°F. A detailed description of the compressor was provided by McGregor (34).

The catalyst bed, recycle loop, and recycle pump, were enclosed in a heated fluidized sand bath to maintain a constant temperature throughout the apparatus. The fluidized sand bath was heated by three sources. The steel wall of the sand bath was heated by 12 strip heaters bolted longitudinally on the outside. This 1.5 kilowatt energy source was controlled manually by supplying variable amounts of power from a power

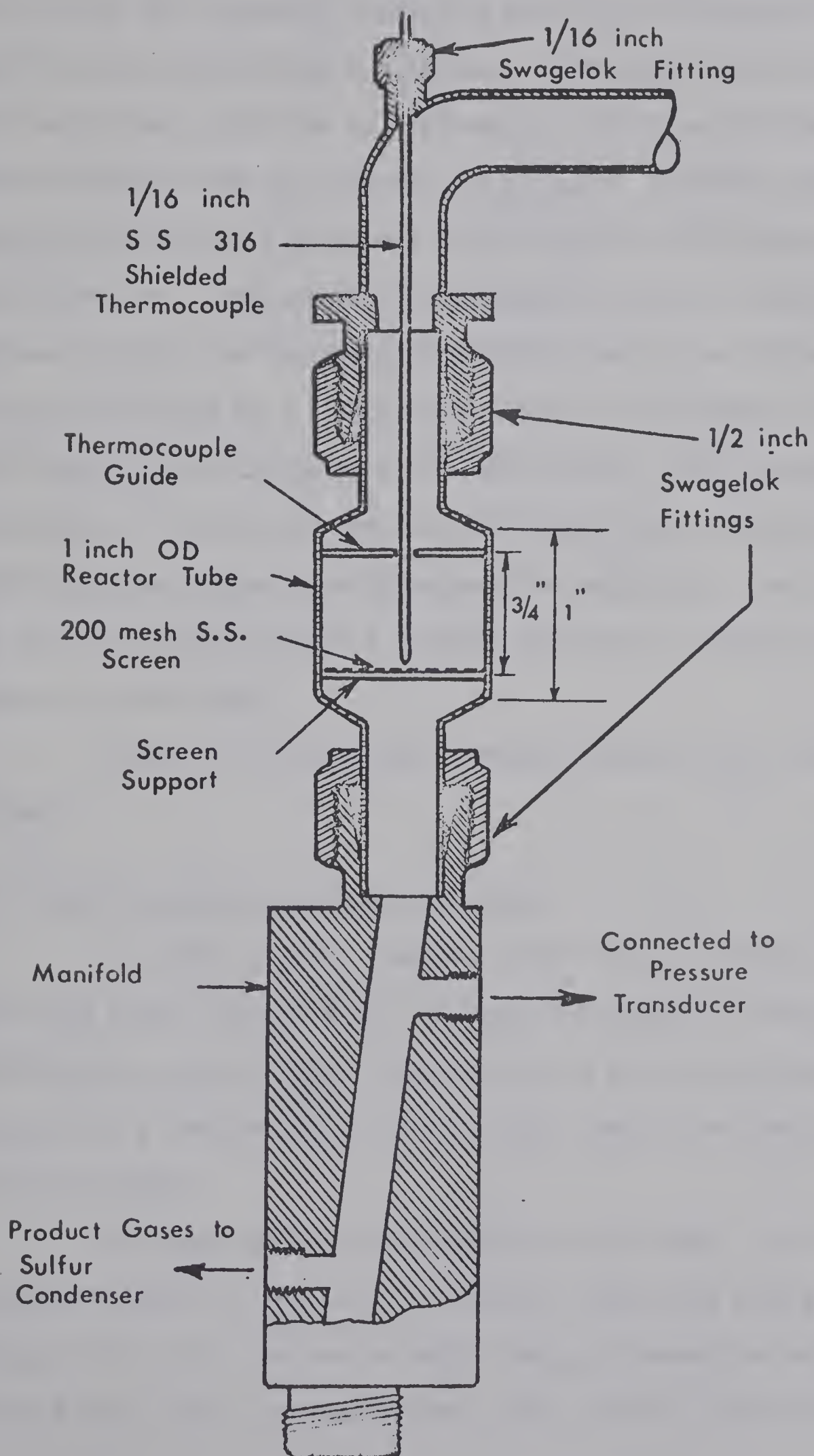


Figure 3-1 Modified Reactor

supply. The strip heaters and outside wall of the sand bath were enclosed by a 2 inch thick asbestos insulation wall. The fluidizing air to the sand bath was preheated by a 6 kilowatt Chromalox immersion heater. This heater was controlled by a Chromalox AR-5514 on/off thermostat. A second heater on the air line was a 3 kilowatt Chromalox immersion heater controlled by a Honeywell R7161 controller with proportional and reset controls. This controller operated to maintain a constant air temperature into the fluidized sand bath. The air was dispersed at the bottom of the bath by a 2 inch thick layer of 5 millimeter diameter glass beads held in place by a fine mesh screen. This arrangement caused the sand to fluidize over the pump and recycle loop, and maintained a nearly constant temperature throughout the apparatus. The air leaving the bath was passed through a cyclone separator to remove any sand that had been carried over.

Figure 3.2 includes the schematic layout of the entire reactor assembly.

3.3 Feed Preparation and Metering System

In order to allow complete flexibility of reactant concentrations and ratios, the feed gas was mixed continuously from separate bottles of N_2 , H_2S and SO_2 . This required a feed system capable of maintaining a constant flow and a constant composition for the course of an experiment.

The gases were discharged from the cylinders at a constant pressure by means of regulators. Each gas stream was then passed through a 500 cubic centimeter bed of $CaSO_4$ to remove any moisture (liquid water tends to catalyse the Claus reaction, particularly on

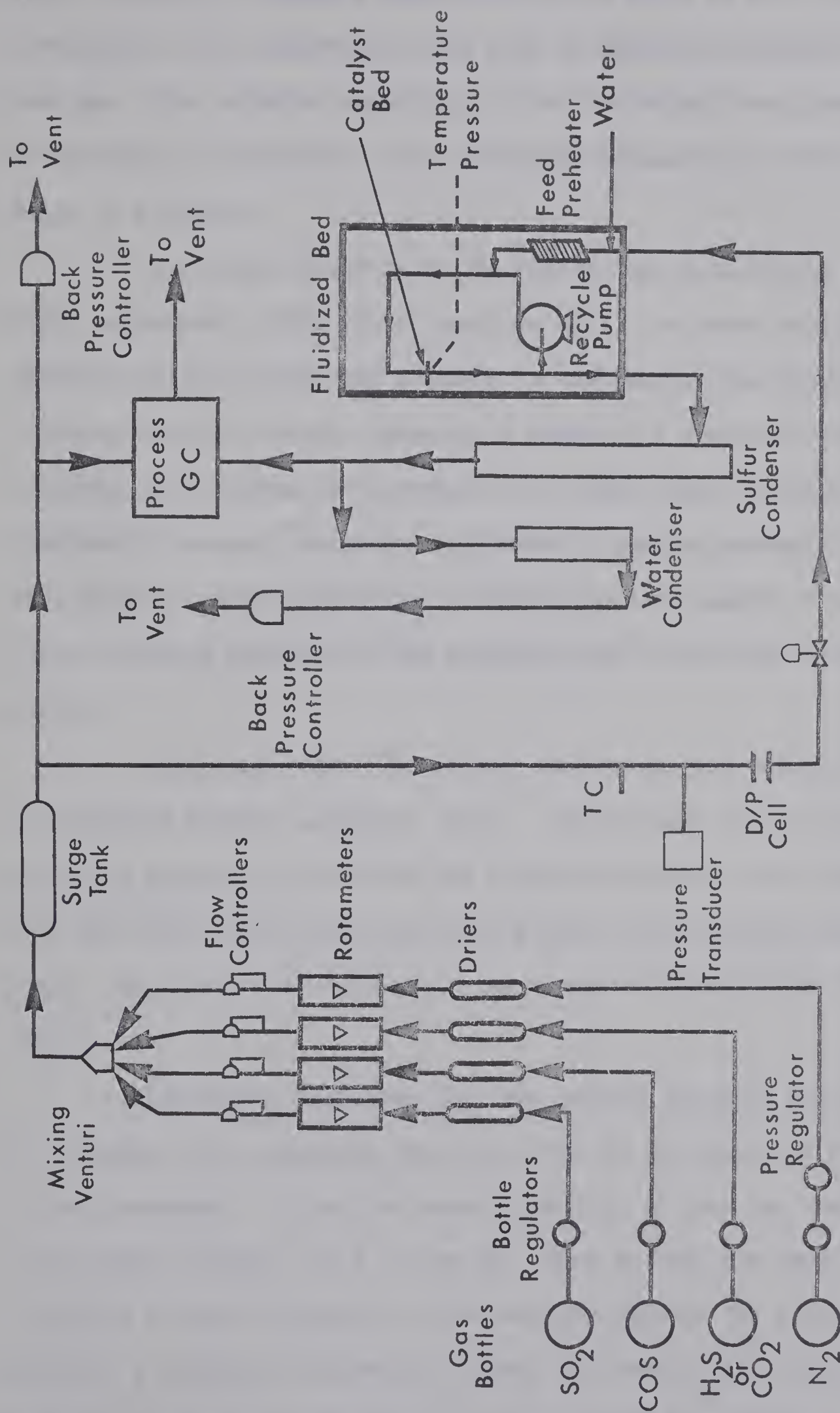


Figure 3-2 Schematic Flow Diagram of Modified Experimental Equipment

glass surfaces). Separate needle valves and Moore 63 BU-L constant differential flow controllers were used to maintain constant flows for each gas. The relative magnitudes of the individual feed gases could be observed on rotameters. The individual streams were then mixed by means of a venturi.

The total feed flow to the reactor was measured by a Foxboro 613 PL electronic differential pressure cell. In order to maintain a constant and known flow the pressure in the feed system above the orifice was held at a steady pressure by means of a pressure relief valve. A Foxboro 62 H controller operated on an input from a Foxboro 66 FR-2 electronic pressure transducer to control a Foxboro automatic valve. This pressure relief system bled off the required amount of gas to maintain a constant pressure on the upstream side of the flow measuring orifice.

The actual feed flow to the reactor was set manually by an air operated Foxboro automatic valve. The pressure relief system automatically adjusted to maintain the desired pressure in the feed system. This made feed rate changes possible without upsetting the feed composition. This system required that some bleed-off occurred at all feed rates.

Experience indicated that the reactor pressure was influenced by a dynamic flow behaviour resulting from the condensation of sulphur in the condenser. It was far more acceptable to have the reactor pressure change slightly, (0.5-1.0 mm Hg), than to have the feed rate change. Therefore a Foxboro automatic valve was employed on the product line to maintain a constant differential across the feed orifice meter. This automatic valve was controlled by a Foxboro 625 M controller.

By holding all these disturbances, affecting feed flow and composition, to a minimum it was possible to maintain a set steady state indefinitely. Figure 3.2 shows the entire feed system. Figure 3.3 illustrates the control scheme of the automatic valve systems.

In order to obtain a wide variation in H_2O concentration in the reactor, provision was made to add an H_2O feed stream to the reactor loop. Distilled water was added at a variable rate by means of a Sage Model 355 syringe pump with a 50 cubic centimeter syringe. This particular pump was chosen due to the wide variation of rates possible (0.0034 cc/min to 86 cc/min with a 50 cc syringe). The liquid water was vaporized in an 18 inch coil of 1/8 inch stainless steel tubing enclosed in the fluidized sand bath. The vaporized H_2O was added to the N_2 , H_2S and SO_2 stream by means of a "T" connection just prior to the reactor loop. The feed rate of the water was determined, by a calibration of the syringe pump. This calibration is included as section 3 of Appendix A.

3.4 Sampling System

The sampling system enabled the gas chromatograph to analyse the feed and the product streams alternately.

The product stream was passed through a sulphur condenser to avoid sulphur deposition in the chromatograph columns and detector filaments. The condenser is shown in detail in Figure 3.4. It was maintained at a temperature above the solidification point of sulphur by Nichrome wire heaters. The wire was wrapped around the outside of the condenser in such a way that a gradual decrease of temperature occurred from inlet to outlet. This insured that the bulk of the sulphur remained

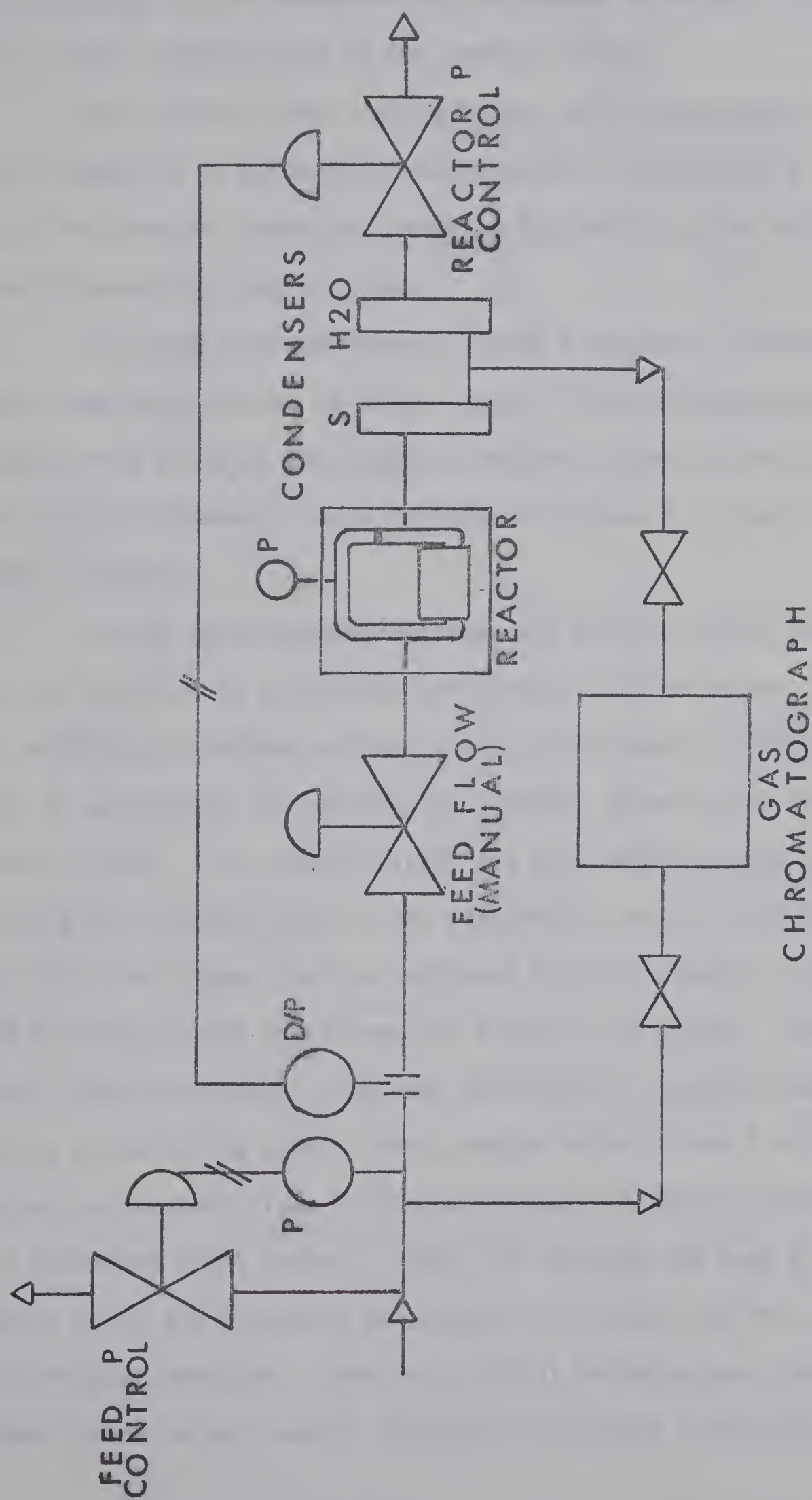


FIGURE 3-3: FEED SYSTEM CONTROL SCHEME

in the liquid phase and flowed down the condenser to the sulphur accumulator. The top of the condenser was maintained at about 110°C to insure that no water condensed out of the product stream.

The product lines leading to the gas chromatograph were heated by wire wrappings to avoid water condensation. Since only a small portion of the product stream was required for analysis, the bulk of the stream bypassed the sample system.

The bypass stream flowed through a condenser, operated at the ambient room temperature, to remove water. This was necessary to keep the water from plugging the reactor pressure control valve and the vent lines. This condenser is also included in Figure 3.4 along with the sulphur condenser.

Inside the chromatograph oven the desired stream (product or feed) was selected by a solenoid operated air slider valve. To allow this switching to be made without upset to the reactor flows, a certain amount of adjustment was required to 5 needle valves prior to beginning a series of runs. The needle valves and both modes of flow are shown in Figure 3.5. Needle valve C was adjusted to provide 1 in. of Hg pressure within the sample loop as indicated by the manometer. Needle valves A and B were adjusted to balance the flows to the system. The existence of equal feed and product flows was detected by a constant manometer pressure on switching modes. Next, needle valves D and E were adjusted to maintain constant flows of the two streams if they were being sampled or if they were being vented. Again this balance was made by switching selector modes and observing the reaction of either the feed pressure, or the reactor pressure. Once this initial balancing was complete no further attention was usually required to maintain a constant sample

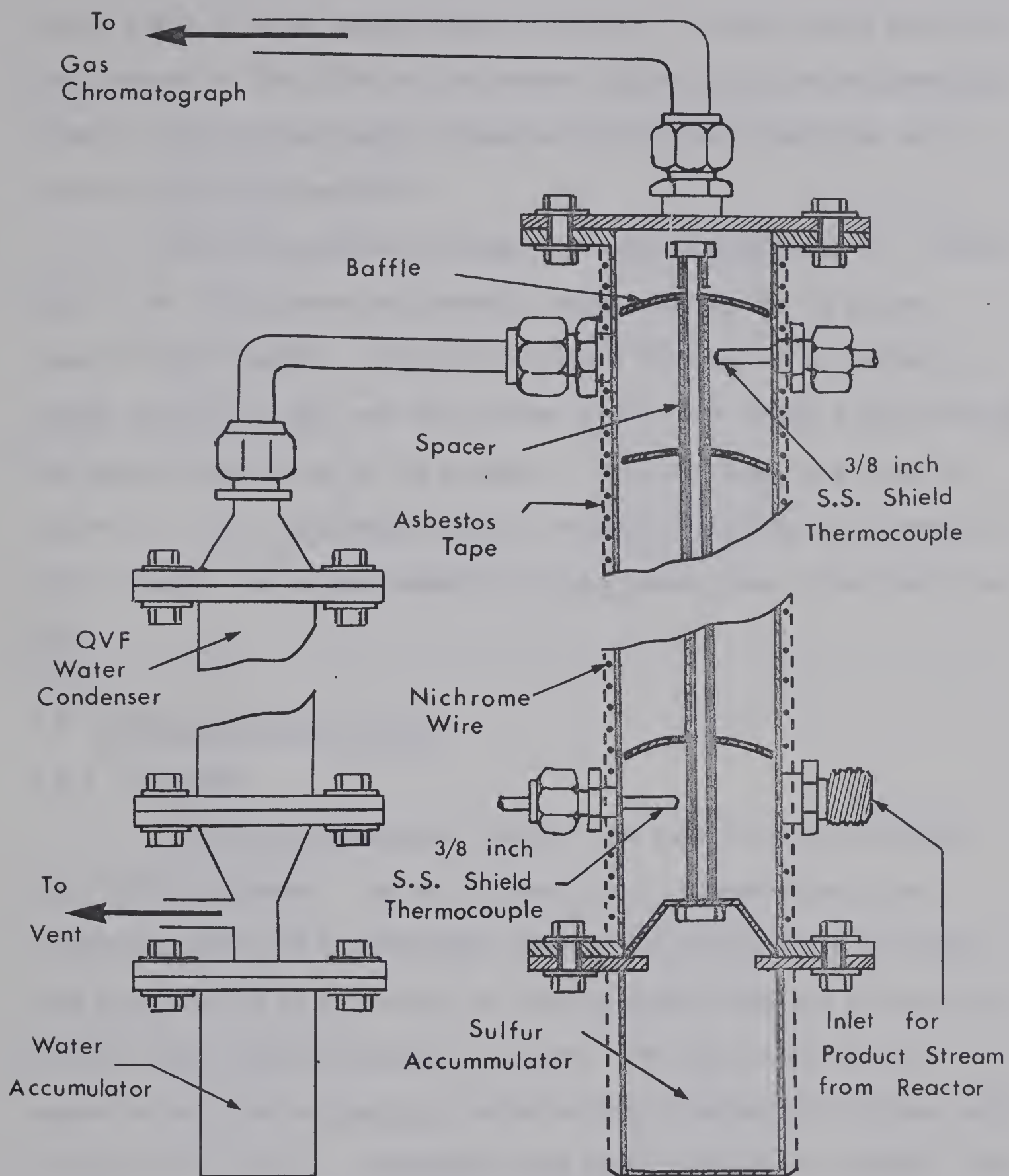


Figure 3-4 Modified Water and Sulfur Condensers

pressure and to allow smooth mode switching. The feed system was such that changes in feed flow to the reactor had no effect on the sampling system, since the two sample streams were withdrawn from areas maintained at constant pressures.

The gas stream being sampled flowed through the 2 c.c. sample loop to the vent system continuously, except during the 15 second "sample inject" period. During this period the sampled stream was routed directly to the vent and the He carrier gas stream flowed through the sample loop and on to the columns. These two modes are shown in Figure 3.5. This injected a constant volume of gas into the chromatograph columns, the volume depending on the sample loop volume and pressure.

3.5 Product and Feed Analysis

3.5.1 Equipment

The gas chromatograph analysis was supervised by a Beckman Model 320C Programmer. The unit controlled 11 cam-operated microswitches by means of a synchronous motor. The cam switches were variable with respect to the length of time they were open and to the time at which they initially opened or closed. The cycle time of the apparatus was also variable by switching either motors or the gear ratio of the drive assembly. Throughout this project the cycle time was left at 6 minutes.

The microswitches were utilized in two ways:

1. to operate a solenoid air valve which provided air pressure to one side or the other of a slider valve,
2. to close an electronic relay and complete an electronic circuit.

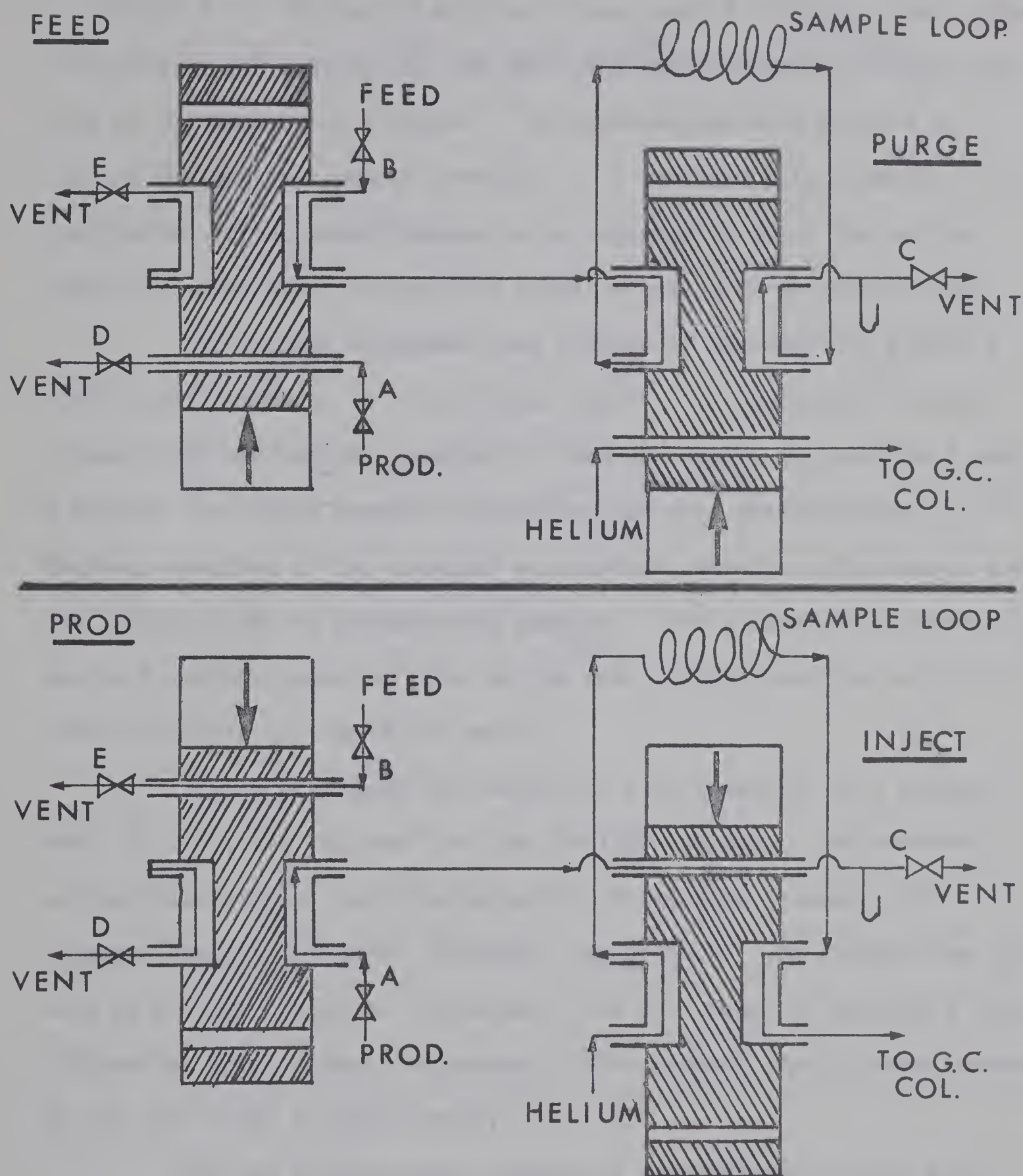


FIGURE 3-5: MODE SELECTION AND SAMPLE INJECTION VALVES

The first way was utilized for sample injection as described in section 3.4. The second application was used for changing the signal attenuation and closing the IBM 1800 interrupt contacts to begin scanning by the monitoring programs. The attenuations were applied by routing the detector output through 1 of 4 ten turn potentiometers. The resistances of the potentiometers were adjusted to apply the desired amount of attenuation to keep the signal within a 20 millivolt range.

The Beckman Programmer was capable of operation in either a single sample mode or in a continuous manner. By operating in a continuous mode the complete analysis of one gas sample was performed every 6 minutes (including computer monitoring and area determination). All that was required of the operator was periodic baseline adjustments and the switching of the stream being sampled. This allowed the operator to devote a maximum amount of time to the rest of the apparatus and still obtain reliable and immediate results.

The chromatograph was monitored simultaneously by a Sargent Model SR millivolt recorder and the IBM 1800 computer. The recorder was equipped with a disc type mechanical integrator; however, the computer analysis was used throughout the project. The recorder was used only as a visual check on the computer and as a means of providing faster information about process adjustments (the computer results were reported at the end of the 6 minute cycle).

The gas chromatograph employed a four filament bridge with separate carrier and reference streams. The filament current was maintained at 320 m.a. and both He flows were adjusted to 40 c.c. per minute by means of separate needle valves. The columns, detector, sampling valve, and stream switching valve were enclosed in a single temperature

controlled oven.

3.5.2 Chromatographic Columns for the Analysis of Sulphur Gases

A typical plant stream could include N_2 , CO_2 , COS , H_2S , SO_2 , H_2O , and CS_2 . One objective of this research project was to develop a method of analysis which would provide quantitative measurements of all of these components. However, since this analysis was more complicated than the analysis of N_2 , H_2S , SO_2 and H_2O required for the kinetic measurements, it was not used extensively in this project.

3.5.2.1 Analysis of N_2 , H_2S , SO_2 and H_2O

An analysis of the four components of interest to this project, N_2 , H_2S , SO_2 , and H_2O , was carried out isothermally and without back-flushing. The He carrier and reference flows were both held at 40 c.c. per minute. The columns and detector were maintained at 225°F. Higher temperatures caused a fusing of the SO_2 and H_2O peaks, while lower temperatures resulted in increased H_2O tailing. The two columns were 1/8 inch thin walled stainless steel tubing. The first column was packed with Chromosorb 104 and was 4 feet long. The second column was packed with Porapak Q-S and was 6 feet long. The complete analysis was carried out in the two column flow mode. No attempt was made to optimize the length of the Porapak Q-S column. Shorter Chromosorb 104 columns did not give adequate separation of SO_2 and H_2O , while longer columns caused increased H_2O tailing.

The analysis of one sample was easily carried out in less than 6 minutes. A computer plot of the signal received by the computer is shown in Figure 3.6. The N_2 peak for this analysis, and all the other analyses that follow, has been attenuated 120 times. All the other peaks are not attenuated.

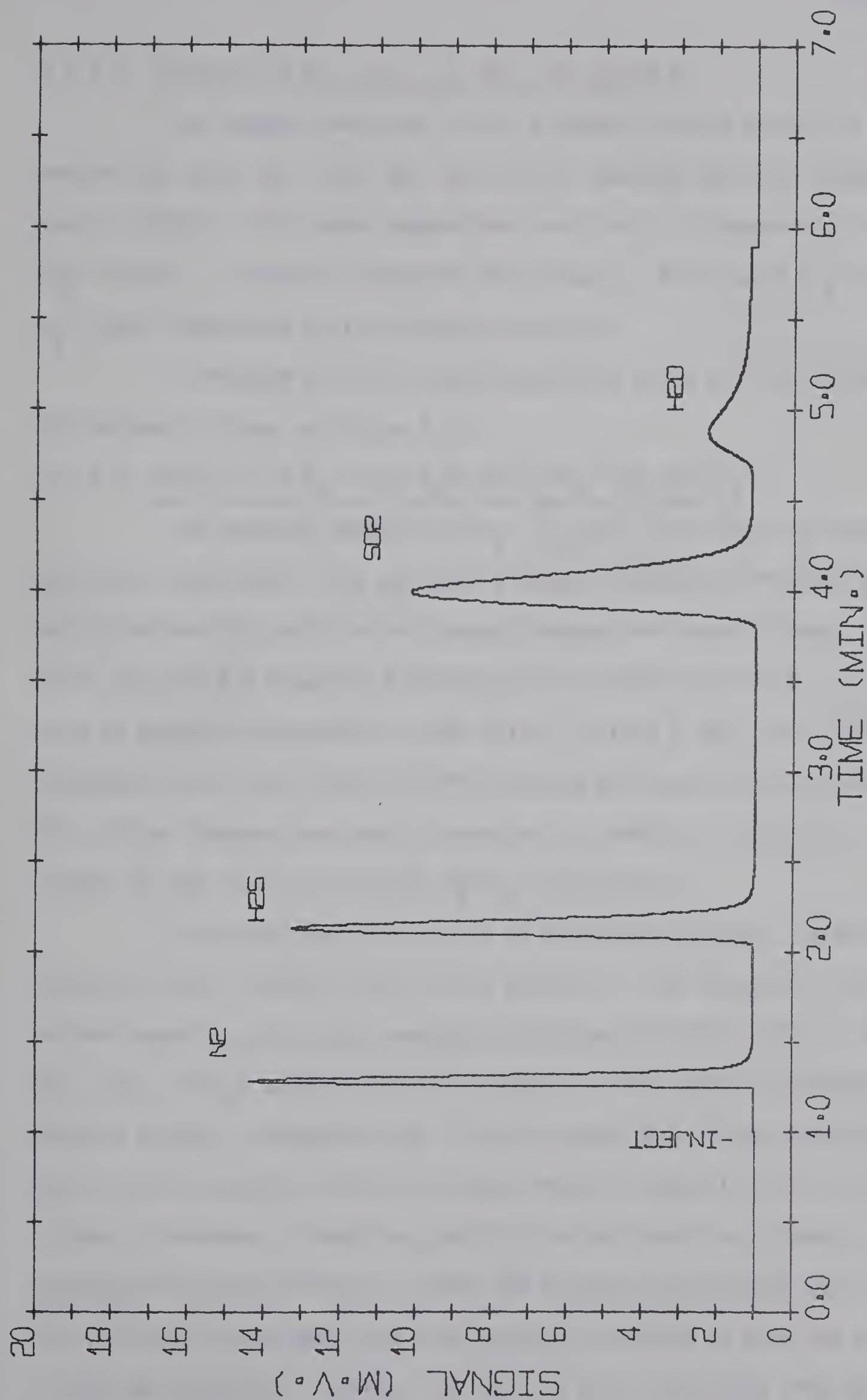


FIGURE 3-6
4 FOOT CHROMOSORB 104 AND 6 FOOT PORAPAK Q-S

3.5.2.2 Analysis of N_2 , CO_2 , H_2S , COS , SO_2 and H_2O

The columns described in the previous section were used to analyse N_2 , CO_2 , H_2S , COS , SO_2 , and H_2O by lowering the oven temperature to 180°F. This lower temperature resulted in increased H_2O and SO_2 tailing. A shorter Chromosorb 104 column, 3 feet, gave SO_2 and H_2O peaks comparable to the previous analysis.

A computer plot of a sample analysis using a 4 foot Chromosorb 104 column is shown in Figure 3.7.

3.5.2.3 Analysis of N_2 , CO_2 , H_2S , COS , SO_2 , H_2O and CS_2

The complete analysis of N_2 , CO_2 , H_2S , COS , SO_2 , H_2O and CS_2 was more complicated. CS_2 was very strongly adsorbed on Porapak Q-S and therefore CS_2 could not be passed through the second column. As well, CS_2 and H_2O required a Chromosorb 104 column of 6 feet to provide an adequate separation. When using a column 6 feet long, the temperature must be at least 210°F to avoid tailing of the CS_2 and H_2O . This higher temperature made it necessary to employ a Porapak Q-S column 10 feet long to separate N_2 - CO_2 and H_2S - COS .

The actual analysis of all of these gases was not carried out. However, it was verified that it was possible. The Chromosorb 104 column passed N_2 , CO_2 , H_2S , and COS through with little affect. The SO_2 , CS_2 , and H_2O eluted from this column, in that order, beginning at about 4 minutes. Meanwhile the 10 foot Porapak Q-S column separated N_2 , CO_2 , COS , and H_2S within 3 minutes from the injection into the first column. Therefore it would be possible to use these two columns to separate the entire mixture. After the N_2 , CO_2 , H_2S and COS had eluted from the two column mode, the flow could be switched so that the second column was bypassed. The SO_2 , CS_2 and H_2O would the elute from the

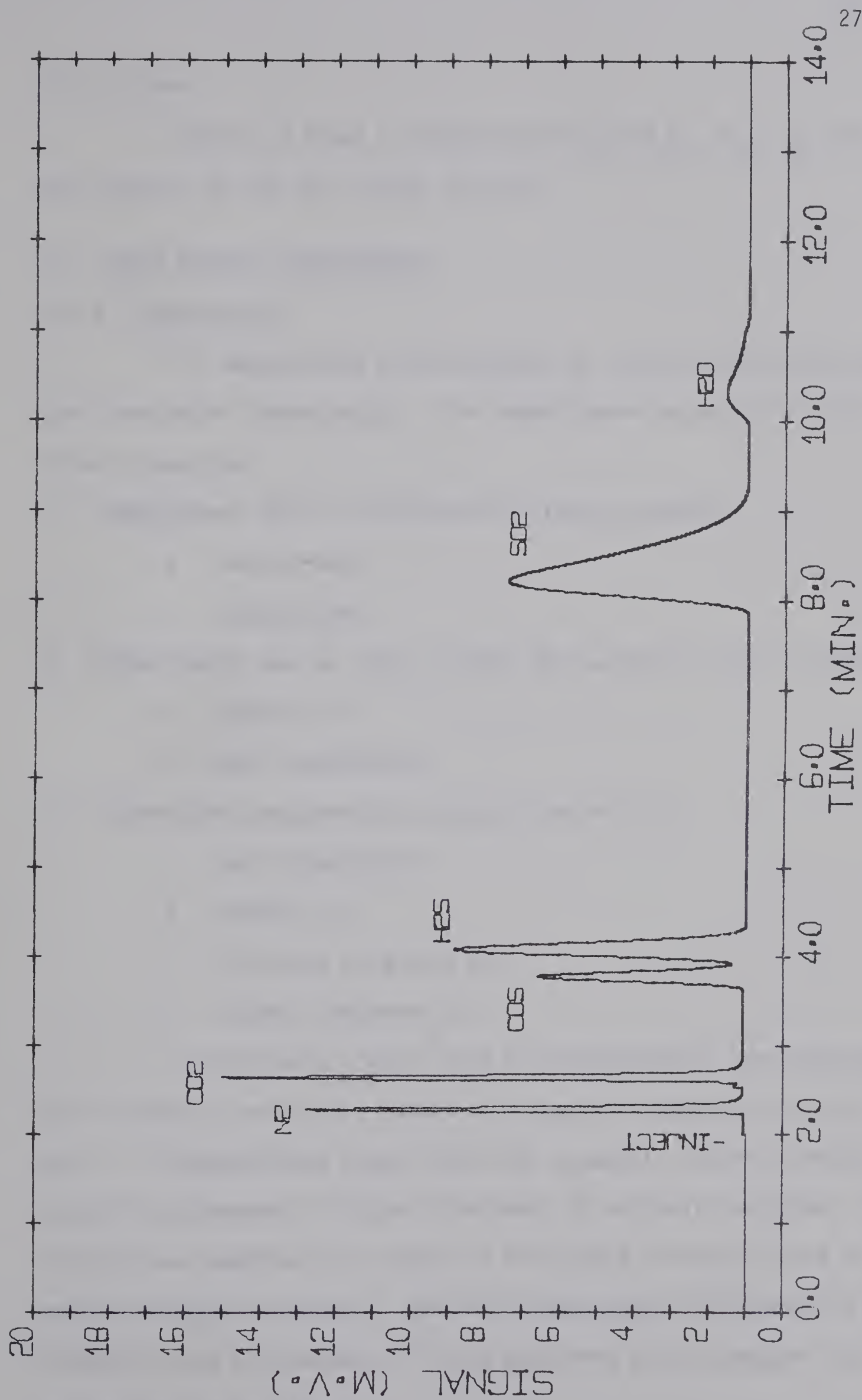


FIGURE 3-7
4 FOOT CHROMOSORB 104 AND 6 FOOT PORAPAK Q-S

first column.

Figure 3.8 shows a computer plot of the N_2 , CO_2 , H_2S , and COS analysis on the two columns at $210^\circ F$.

3.6 Other Process Measurements

3.6.1 Temperatures

All temperatures were monitored by stainless steel shielded iron-constantan thermocouples. The temperatures measured fall into three categories:

1. Temperatures used to calculate the kinetic results
 - a. reactor wall
 - b. catalyst bed
2. Temperatures used as input signals for automatic control devices
 - a. preheat air
 - b. gas chromatograph
3. Temperatures measured for display purposes only
 - a. gas chromatograph
 - b. preheat air
 - c. fluidized sand bath (2)
 - d. sulphur condenser (2)

The millivolt signals from the thermocouples were referenced to ice point by means of a common cold junction immersed in an ice bath. All temperatures except those for automatic control were displayed by a Honeywell 24 point Electronik 16 millivolt recorder. The recorder was operated at a span of 5 millivolts for taking data to provide maximum resolution. The two thermocouples of interest in data reduction were also capable of being monitored by the computer for on-line data acquisition.

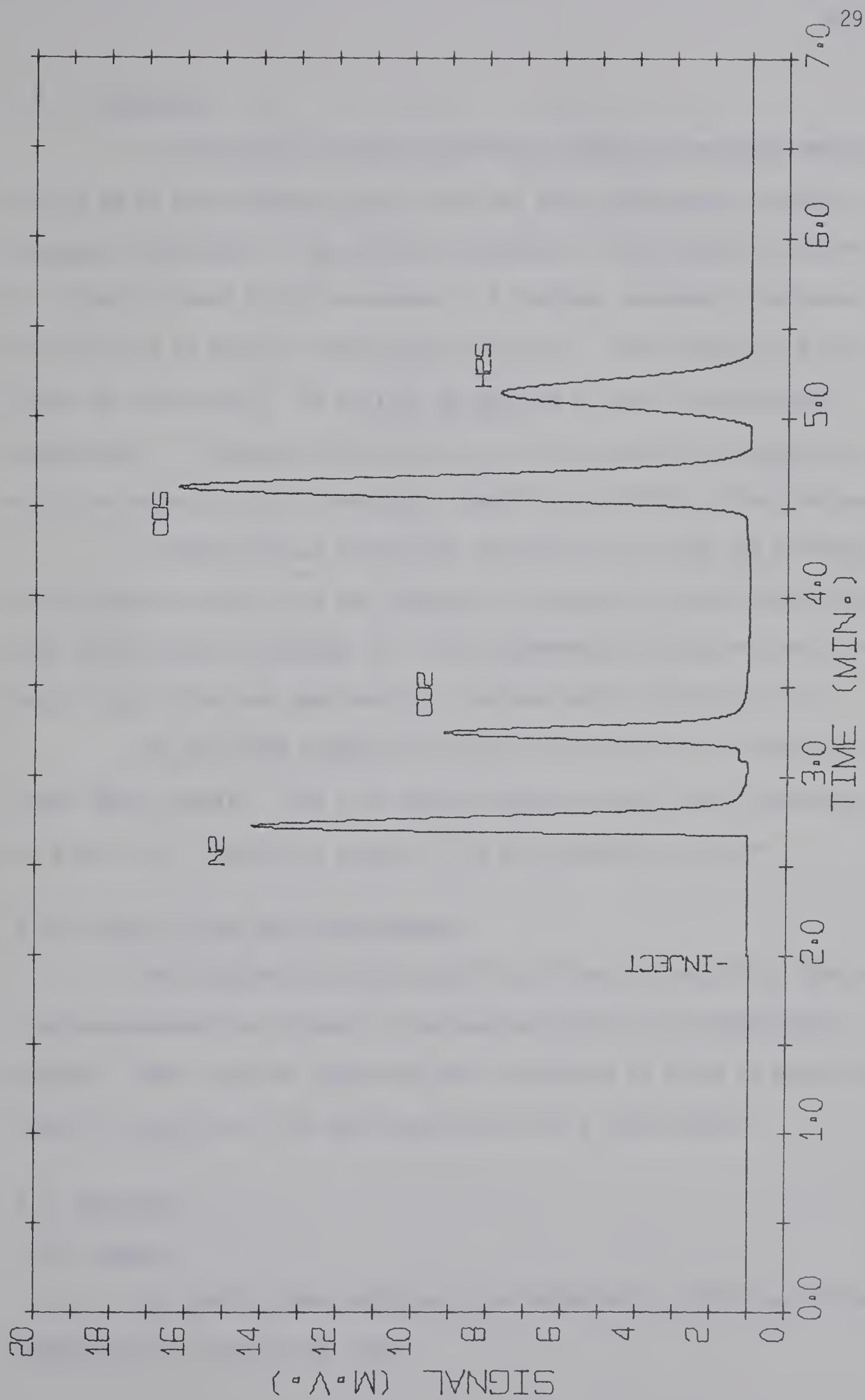


FIGURE 3-8
5 FOOT 104 AND 10 FOOT Q-5

3.6.2 Pressures

A Foxboro HF electronic control three pen recorder monitored the 10 to 50 milliamper signals from the feed and reactor absolute pressure transducers. The absolute pressure of the feed was measured by a Foxboro Model 611AH transducer. A Statham pressure transducer was utilized to measure the reactor pressure. This particular transducer was used due to its ability to operate at the fluidized bath temperature. A Foxboro 693 AR EMF to current converter was used to make the output of this transducer compatible with the Foxboro recorder.

A Foxboro 625 M single pen controller utilized the differential pressure reading for the purposes of controlling the reactor pressure as outlined in section 3.3. The differential pressure across the feed flow orifice was measured by a Foxboro Model 613 DL D/P cell.

The IBM 1800 computer also had the capability of monitoring these three signals. The 0 to 50 milliamper signals were converted to 0 to 5 volt signals by means of 100 ohm dropping resistors.

3.6.3 Role of the IBM 1800 Computer

The computer had the capability of monitoring all of the process measurements of interest simultaneously with the conventional devices. This parallel operation was introduced to allow an easy transition to complete on-line data acquisition at a future date.

3.7 Materials

3.7.1 Gases

H₂S and SO₂ were obtained from Matheson Co. with the following specifications provided by them

SO_2	99.98%	(anhydrous grade)
H_2S	99.50%	(C.P. grade)

These gases were further analysed by gas chromatograph with the typical results shown in Table 3.1.

TABLE 3.1
GAS PURITIES

<u>gas</u>	<u>impurities</u>	<u>estimated amount</u>
SO_2	H_2O	slight traces (less than 0.02%)
	N_2	
	H_2S	
H_2S	N_2	trace
	CO_2	0.10 mole %
	H_2O	0.20 mole %

N_2 was obtained from Linde Co. Ltd. The specified purity was 99.996%. Each new bottle was analysed by gas chromatography to check for O_2 impurities. If any O_2 was detected the bottle was not used (observance of an O_2 peak was interpreted as an O_2 content exceeding 0.05 mole percent).

3.7.2 Catalyst

The bauxite catalyst was obtained from Minerals and Chemicals Phillips Corporation of New Jersey. It was designated as Porocel Sulphur Recovery Catalyst. The manufacturer provided the following specifications.

TABLE 3.2
POROCEL SULPHUR RECOVERY CATALYST

Volatile material	6%
Chemical composition (volatile free basis)	
Al_2O_3	89.0%
Fe_2O_3	5.0%
TiO_2	2.8%
SiO_2	2.6%
insol.	0.6%
Surface area	215 m. ² /gm

This catalyst was obtained from the same batch as that used by McGregor (34).

3.8 Experimental Procedures

3.8.1 General

The general operation of the equipment was essentially the same as that of McGregor (34) and Liu (31). The same precautions were taken to insure stability of the process measuring devices and the thermal stability of the reactor and fluidized sand bath. As a general rule, the sand bath and other equipment were allowed a 24 hour warm up period after a complete start up.

In order to avoid this lengthy stabilization period, the complete system was maintained in a ready state between runs. The first data point then required a 45 minute thermal stabilization period with the initial pump start up and upset of thermal stability caused by the reaction. Successive data points could be taken at different steady

states with 15 minute stabilization periods.

3.8.2 Initial Feed Adjustments

As outlined in section 3.3 changes were made to the existing feed system to provide better stability. Before starting the initial reaction, certain adjustments were necessary to obtain a stable feed flow. These adjustments were made while flowing N_2 through the system prior to turning on the H_2S and SO_2 .

First the amount of feed bleed-off was adjusted, so that at the maximum feed rate to be reached in the planned set of experiments, a small amount of bleed-off always occurred. The actual pressure maintained by the bleed-off system was checked by a mercury manometer to insure that the pressure used for the D/P cell calibration was maintained (22.5 psia). The N_2 flow was then adjusted to the approximate amount required for the first data point.

The reactor pressure control system was then adjusted to provide the desired reactor pressure. For this adjustment the recycle pump was turned on. The reactor pressure was set by a controller utilizing the feed flow as an input. The controller adjusted an automatic valve to maintain the feed flow determined by the controller setpoint. The reactor pressure was therefore set by simultaneously making adjustments to the manual feed flow valve and the controller setpoint until the desired combination of feed flow and reactor pressure was obtained.

The final adjustment involved balancing the sampling system flows as described in section 3.4.

Once these adjustments were made the reactant gases were turned on and adjusted to yield the desired reactant concentrations. Since the

reactant gases made up a small part of the total flow no further adjustments were necessary.

3.8.3 Changing Steady States

Successive data points were taken by changing steady states in one of two ways:

1. the feed flow to the reactor was changed but the reactant concentration was maintained constant
2. the reactant concentration was changed and the feed flow was maintained constant.

The first method required a manual change of the feed flow valve and subsequent adjustment of the reactor pressure controller setpoint to obtain the desired reactor pressure.

The second method required only changes to the appropriate reactant needle valves.

Generally, a normal steady state change would only introduce a slight thermal upset in the system. The reactor temperature was adjusted to the desired temperature by a slight change to the setpoint of the controller on the second air preheater. By bringing about a slight change in the air temperature the desired reactor temperature could be obtained.

3.8.4 New Catalyst - Cold Start Up

In order to load a new catalyst charge or perform maintenance on the reactor system, the fluidized bath was cooled down for 6 to 8 hours. The sand was drained from the bath and the asbestos wall and steel wall removed. The catalyst holder was easily accessible by disconnecting the appropriate Swagelok tube fittings.

The catalyst holder was emptied and thoroughly cleaned by high pressure air. The new pre-weighed catalyst charge was then placed on the holder screen. The catalyst was then overlaid with a layer of 3/32 and 1/16 inch stainless steel balls. Any fittings which had been loosened were then coated with an anti-seizing agent (Silver Goop) and rejoined. The recycle assembly was pressure tested and any leaks fixed.

The sand bath was then reassembled and the air turned on. The three heat sources were switched on and set at the appropriate settings.

To insure reproducible catalyst activity, each new catalyst batch was pretreated according to the following procedure:

1. N_2 was passed through the catalyst bed for 24 hours. During this period the temperature was maintained at $250^\circ C$.
2. A mixture of 6% H_2S in N_2 was passed through the catalyst bed for 6 hours at $250^\circ C$.
3. A mixture of 5% H_2S and 2.5% SO_2 in N_2 was reacted at $250^\circ C$ and a reactor pressure of 830 m.m. Hg for 2 to 4 hours.

3.9 Data Acquisition and Reduction

The MPX Operating System and the DEC 680 Communications System allowed the raw data to be processed to kinetic results essentially in an on-line mode on the IBM 1800 Computer.

At the end of each gas chromatographic analysis the results were available immediately on the laboratory teletype. The temperatures and pressures were available from either the strip chart recorders or from the computer DDC files.

Once the feed composition had been analysed two or three times with comparable results, and the feed flow, reactor temperature, and

reactor pressure had remained stable, the gas chromatograph was switched on to perform the product analysis. The product stream was analysed until 2 or 3 successive analyses indicated a steady state. This signalled the end of the data acquisition.

The raw data could then be reduced to kinetic results before a change to a new steady state was made. This procedure eliminated incorrect data points due to human errors in data acquisition, since the reduced kinetic results would generally indicate any gross errors.

The reduction of data was carried out almost instantaneously due to the partitioned core feature of the computer. Under MPX the program was entered into the background processing queue by a simple teletype request. If a batch processing program initiated from the card reader was running, it was swapped to disk and the background program began execution. The order of execution of queued background programs was according to their order of entry into the queue. This generally resulted in execution starting within 1 minute of the initial queue request.

The data reduction program read all of the raw data input through the laboratory teletype. The data was entered in a format free form on request from the program. The program then processed the data and entered the raw and the processed data into user defined disk files. The kinetic results were then output to the teletype in tabular form for quick and simple reference.

Once the reduced data was reported, the operator could change to the next desired steady state or correct any obvious errors. The data were now available to other coreloads used for manipulation and presentation of the data in either tabular or graphical form. The

program listings for these coreloads and a numerical example of the data reduction are included in Appendix C.

IV. EXPERIMENTAL RESULTS

4.1 Experimental Program

Reaction rates were measured at 515°K ($\pm 1^\circ$) and at total reactor pressures between 830 and 850 mm. Hg. The recycle reactor was operated so that the reactant conversions were generally greater than 20 per cent. McGregor (34) had taken data for this reaction under similar conditions but at conversions generally less than 20 per cent.

The data obtained in this study cover three general areas, as follows:

1. moderate conversion (20-60 per cent)
2. high conversion (80-95 per cent)
3. water addition

The moderate conversion runs were performed on two separate catalyst charges, both of approximately 0.5 grams. The water runs were carried out on a third catalyst charge of about the same weight as the first two. The high conversion runs were carried out on a single catalyst charge weighing approximately 3.9 grams.

A summary of the reaction conditions is presented in Table 4.1. A detailed presentation of the raw data and the processed data is given in Appendix C.

4.2 Bulk Mass Transfer Test

For a recycle reactor it is possible to operate at a sufficiently high recycle rate to exclude bulk mass transfer as a rate determining step. Frequently during the data taking, and at every catalyst change, the recycle reactor was tested to ensure that the recycle rate was sufficient for this purpose. This test was quite simple

TABLE 4-1
REACTION CONDITIONS

RUN	CAT WT.	TEMP. (K)	PRESS (MM HG)	FEED COMPOSITION				H2S CONV.
				N2	H2S	SO2	H2O	
1-01	0.5091	515.3	834.2	89.9	7.8	2.1	0.0	11.34
1-02	0.5091	515.3	835.5	89.8	7.5	2.5	0.0	12.43
1-03	0.5091	514.9	836.2	89.2	6.8	3.9	0.0	15.28
2-01	0.5091	514.7	829.7	92.4	3.8	3.7	0.0	22.75
2-02	0.5091	514.9	829.7	92.0	4.0	3.8	0.0	17.74
2-03	0.5091	514.6	834.2	90.8	6.6	2.5	0.0	23.74
3-01	0.5091	515.1	829.7	92.4	3.8	3.7	0.0	31.17
3-02	0.5091	514.2	830.3	92.3	3.8	3.7	0.0	23.63
3-03	0.5091	514.2	829.7	92.3	3.8	3.7	0.0	17.74
3-04	0.5091	514.0	830.3	92.3	3.8	3.7	0.0	15.09
4-01	0.5091	515.3	846.0	92.1	5.0	2.7	0.0	62.39
4-02	0.5091	515.6	840.8	91.6	5.0	3.3	0.0	67.63
4-03	0.5091	513.7	840.8	90.6	5.2	4.0	0.0	64.60
4-04	0.5091	516.5	842.1	90.9	6.3	2.7	0.0	53.14
5-01	0.4946	516.2	842.7	93.1	4.5	2.3	0.0	21.18
5-02	0.4946	515.5	846.0	91.2	6.5	2.2	0.0	20.22
5-03	0.4946	515.3	847.3	90.2	7.4	2.3	0.0	14.96
6-01	0.4946	514.6	846.0	89.1	5.1	5.6	0.0	31.43
6-02	0.4946	514.7	847.3	84.9	9.5	5.4	0.0	23.11
6-03	0.4946	513.5	853.9	91.0	7.7	1.1	0.0	11.56
7-01	0.4946	514.2	847.3	90.5	8.2	1.2	0.0	11.56
7-02	0.4946	514.4	847.3	89.7	8.1	2.0	0.0	21.19
7-03	0.4946	514.2	847.3	88.7	7.6	3.5	0.0	28.04
7-04	0.4946	514.2	847.3	88.0	7.6	4.2	0.0	33.93
7-05	0.4946	514.2	847.3	86.3	7.3	6.2	0.0	36.74
7-06	0.4946	514.7	848.6	81.3	8.7	9.8	0.0	41.19
8-01	0.4946	514.4	847.3	85.5	4.3	10.1	0.0	53.48
8-02	0.4946	514.4	847.3	87.4	4.0	8.4	0.0	44.86
8-03	0.4946	514.4	848.6	91.0	4.2	4.6	0.0	35.04
8-04	0.4946	514.4	844.7	91.8	5.4	2.7	0.0	24.60
8-05	0.4946	515.1	847.3	93.0	5.4	1.5	0.0	16.33
9-01	0.5091	515.8	840.8	92.1	5.3	2.4	0.0	40.66
9-02	0.5091	515.1	840.8	86.9	4.9	2.3	5.6	31.07
9-03	0.5091	514.9	840.8	81.9	4.7	2.2	11.0	26.50
10-1	0.5091	514.2	834.2	90.8	6.5	2.6	0.0	21.43
10-2	0.5091	513.8	834.2	87.4	6.9	2.4	3.1	15.83
10-3	0.5091	513.8	835.5	84.6	6.9	2.4	5.8	14.39
10-4	0.5091	513.8	832.3	82.8	6.0	2.5	8.4	11.66
10-5	0.5091	514.9	832.9	80.3	6.0	2.7	10.9	8.93
11-1	0.5091	515.3	839.5	90.0	5.2	4.7	0.0	30.17
11-2	0.5091	514.9	836.2	87.1	5.0	4.5	3.1	23.13
11-3	0.5091	515.3	834.2	84.9	4.8	4.2	5.9	17.70

TABLE 4-1 (CONT D)
REACTION CONDITIONS

RUN	CAT WT.	TEMP. (K)	PRESS (MM HG)	FEED COMPOSITION				H2S CONV.
				N2	H2S	SO2	H2O	
11-4	0.5091	514.9	832.9	82.5	4.7	4.1	8.5	14.09
11-5	0.5091	514.9	832.3	78.1	4.5	3.9	13.3	10.90
12-1	0.5091	515.3	832.3	91.9	5.3	2.6	0.0	21.92
12-2	0.5091	515.5	834.2	89.1	5.1	2.5	3.1	16.83
12-3	0.5091	515.3	834.2	86.4	5.1	2.4	5.9	12.85
13-1	3.8684	515.1	829.0	95.1	3.6	1.1	0.0	62.97
13-2	3.8684	515.1	829.7	94.8	3.6	1.5	0.0	84.82
13-3	3.8684	514.0	829.0	93.6	4.2	2.0	0.0	89.01
13-4	3.8684	515.1	770.1	92.8	4.0	3.0	0.0	93.26
13-5	3.8684	515.5	835.5	90.3	3.9	5.7	0.0	94.31
14-1	3.8684	515.3	827.7	93.0	4.8	2.1	0.0	84.83
14-2	3.8684	515.6	829.7	93.1	4.7	2.1	0.0	81.83
14-3	3.8684	515.1	829.0	93.2	4.6	2.1	0.0	79.26

due to a variable speed drive on the recycle pump.

A steady-state conversion was measured at a low circulation rate, and then the circulation rate was increased stepwise until the pump was operating at the highest rate. A conversion independent of the recycle rate indicated that bulk mass transfer had no influence on the reaction rate.

One such test, carried out on a catalyst charge of 0.5091 grams and a total volumetric feed rate of 8.410 standard cubic feet per hour, is included as Table 4.2.

TABLE 4.2
BULK MASS TRANSFER TEST

Pump Setting	Product Concentration		
	N ₂	H ₂ S	SO ₂
4.0	91.31	6.98	1.69
	91.30	6.99	1.70
7.5	91.30	6.98	1.70
	91.32	6.95	1.71

4.3 Effect of Higher Water Concentrations

The water addition runs indicated the same retardation effect observed by McGregor (34) and Hammar (22). A typical water addition run is illustrated in Figure 4.1. The highest conversion was measured without water addition to the feed. Subsequent points were taken with increasing amounts of water added to the feed. (The feed compositions for this run shown in Figure 4.1 are contained in Table 4.1 as runs 10-1 to 10-5.) No attempt was made to adjust the H₂S and SO₂ feed

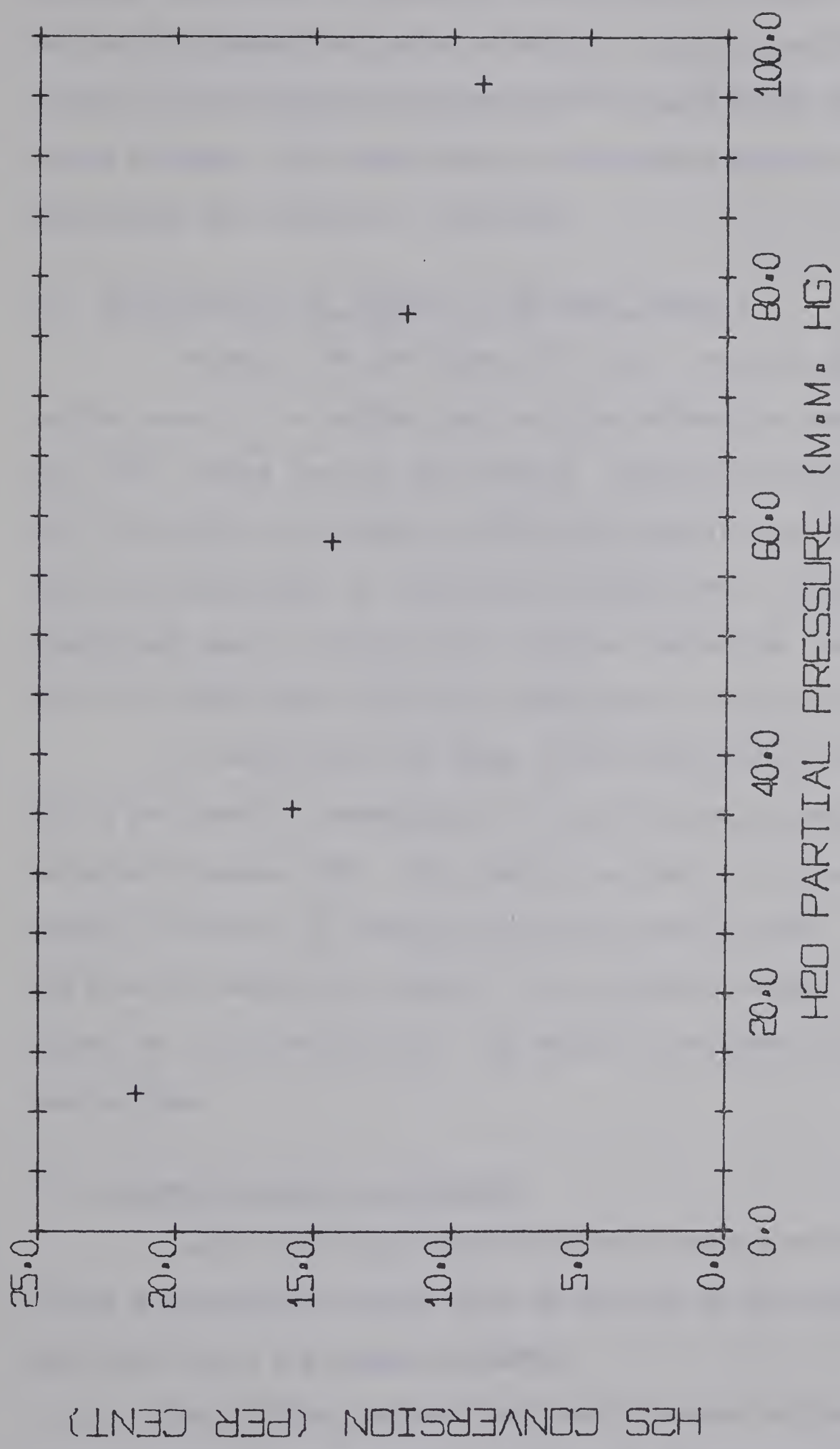


FIGURE 4-1
WATER ADDITION TO FEED

rates to maintain the reactor partial pressures of these components constant throughout the series of points. In all cases these concentrations for the points with water addition were higher than for the points without. This meant that the retardation effect of water was even larger than Figure 4.1 indicates.

4.4 Determination of Sulphur in the Used Catalyst

McGregor (34) and Hammar (22) both concluded that the external surface area of the catalyst was the rate determining area, rather than the total surface area of the catalyst. McGregor performed experiments with different sized catalyst pellets and demonstrated that the reaction rate was proportional to the external surface area. Hammar observed no significant drop in reaction rate when he lowered the reaction temperature to a level where capillary condensation of sulphur would occur.

To verify that the pores of the used catalyst contained sulphur a wet chemical determination was carried out according to an accepted procedure (44). The catalyst had been in the reactor for a number of runs but no serious deactivation had occurred. Prior to cooling down the reactor for removal of the catalyst charge, the reactor was purged for two hours with N_2 . The analysis indicated 2.0 weight per cent sulphur.

4.5 Systematic Errors in the Data

Late in the experimental program a serious error was detected. It was discovered that about 30 to 40 per cent of the measured conversion was occurring in the sulphur condenser.

The sulphur condenser was used to remove the sulphur from the product stream to allow analysis by the gas chromatograph. The condenser

has been illustrated in Figure 3.4 of section 4, chapter 3. The temperature in the condenser ranged from 140°C at the inlet to 110°C at the outlet. It was absolutely necessary to insure that no water condensed from the product stream since liquid water catalysed the reaction. The condenser was designed to provide continuous operation by maintaining most of the sulphur in the liquid phase, thus enabling it to flow by gravity to a heated accumulator pot.

The existence of a reaction in the sulphur condenser was verified by passing a dry stream of N_2 , H_2S , and SO_2 through the condenser operated at the normal temperatures. The gas chromatograph analysis of the product stream detected a water peak not observable in the feed. As well, a material balance indicated that two moles of H_2S were consumed for each mole of SO_2 .

To verify that the observed conversion was not due to the homogeneous reaction a series of tests were carried out. By heating the sulphur condenser to 170°C and passing N_2 through it for 24 hours, a large portion of the sulphur was removed. After this time the condenser temperature was lowered to the normal operating level and a dry N_2 , H_2S , and SO_2 stream was passed through. A reaction was again observed but to a much smaller extent. By disassembling the condenser and heating it at 200°C for 24 hours, all of the remaining sulphur was removed. No reaction was observed using this clean condenser. Earlier workers (34,46) had also found that the homogeneous reaction did not occur at the temperatures used in this study.

Under the right conditions a test for homogeneous reaction would have caused the previous workers to observe the catalytic effect of liquid sulphur condensation. Unfortunately, McGregor (34) tested

his equipment for homogeneous reaction prior to making any heterogeneous runs. This meant that no sulphur was present in the sulphur condenser. Taylor and Wesley (46) concluded that the reaction did not proceed homogeneously because they were able to correlate reaction rates to the catalyst surface area. They only used two different surface areas and measured reaction rates at two temperatures. At neither temperature was the ratio of reaction rates equal to the ratio of surface areas. However, the average of the ratios at the two temperatures agreed with the ratio of the surface areas. (The individual points varied from the average by $\pm 30\%$.) Their conclusion does not appear to be justifiable by their results. Also their sulphur condenser was designed to minimize the contact of sulphur and the product gases. This likely minimized the reaction between H_2S and SO_2 in their sulphur condenser.

4.6 Reaction of H_2S and SO_2 in a Liquid Sulphur Medium

In order to confirm that liquid sulphur catalysed the Claus reaction a one pass reactor was used. The reaction vessel was of pyrex glass, therefore, a preliminary test for a possible reaction on the walls was carried out. No reaction was observed between 140 and 160°C.

A 500 m.l. round bottom flask was employed as a reaction vessel. The N_2 , H_2S , and SO_2 mixture was bubbled through the liquid sulphur at a flow rate of 100 m.l. per minute. A reaction between H_2S and SO_2 was detected over the range of 140 to 160°C.

4.7 Summary of Tests for Reaction in the Sulphur Condenser

Table 4.3 presents a summary of the various tests referred to in sections 5 and 6 of this chapter.

TABLE 4.3
CATALYTIC EFFECT OF SULPHUR CONDENSER

Conditions	H ₂ S	Vol.	Feed Composition		
	Conv. (PCT)	Flow Rate	N ₂	H ₂ S	SO ₂
recycle reactor and S condenser	15.09	7.782SCFH	92.37	3.84	3.78
full S condenser	8.49	7.799SCFH	92.42	3.84	3.74
empty S condenser	<1.0	7.800SCFH	92.40	3.80	3.80
clean S condenser	nil	0.5-8.0SCFH	92.50	5.00	2.50
liquid S condenser	≈10.0	100 m.l./min	92.50	5.00	2.50

4.8 Alternate Sampling Methods

A sampling technique very similar to the one used in this study is generally used in industrial plants (28,30). The one difference is the operating temperature of just slightly above 100°C. This means that the sulphur will not remain in a liquid state. However, this also means that the sulphur cannot flow to an accumulator pot and implies that a much larger condenser volume is required to allow continuous operation. Operation of the condenser in this study at temperatures as low as 70°C cut down the extent of reaction but did not eliminate it.

A condenser design which minimizes the contact time of condensed sulphur and the product gases will eliminate the problem. However, such a condenser would not be capable of continuous operation.

4.9 Conclusions

1. The existence of a reaction in the sulphur condenser meant

that the product compositions measured by the gas chromatograph were not the compositions of the recycle reactor stream. Therefore, the reactant rates calculated using this data were in error. For this reason, no attempt was made to fit the data to rate equations.

2. The conclusion reached by McGregor (34) and Hammar (22) that the external surface area of the catalyst was the rate determining area is verified by the existence of sulphur in the used catalyst.

3. The existence of water in the feed stream severely retards the rate of reaction.

4.10 Recommendations

To carry out meaningful kinetic measurements an alternate method of analysis is required. This method of analysis will have to be capable of analysing the product gas stream when it still contains both sulphur and water. To provide the flexibility of the present system of analysis, it should be capable of measuring the gas phase composition of H_2S and SO_2 .

V. IBM 1800 MONITORING OF THE GAS CHROMATOGRAPH

5.1 Introduction

The gas chromatograph was interfaced to the IBM 1800 computer to provide fast and reproducible feed and product analyses with a minimum amount of operator intervention. A completely automatic analysis enabled the operator to devote more time to the rest of the apparatus. The analysis results were available immediately at the end of the analysis for use in the on-line data reduction program described in Appendix C. The computer results were found to be more reproducible than a mechanical disk integrator-recorder system.

Prior to implementing the computer assisted analysis, an extensive study of the computer package was carried out. This study examined the logic and features of the programs to ascertain their value and to correct any errors. Some features of the package covered in this study were not required for the chemical analysis of this project, but were included to make the study general.

The monitoring system operated in a complete real-time mode; that is, it accumulated and integrated the data dynamically. The computer was shared simultaneously by the following facilities:

1. direct digital control
2. infrared monitoring
3. process programs
4. two levels of background processing
5. batch processing

The computer was operated by the Multiprogramming Executive system (MPX) and was served by a Digital Equipment Corporation 680 Communications System. The gas chromatograph package was configured to handle 4

instruments with a total scan rate limit of 32 points per second. Similar monitoring systems have been employed for as many as 60 gas chromatographs (27).

5.2 Hardware Interface

Linking a gas chromatograph to a process computer appears to be quite simple. Chromatographs produce a continuous analog signal easily conditioned to fall within conventional computer analog input ranges. These signals are relatively free of noise and the noise that is present is generally easily distinguished from actual peaks.

The actual interfacing problem is complicated by the following three factors:

1. Some method of computer-operator two way communication is necessary.
2. Chromatograph signals generally cover a wide range of analog signals during an analysis.
3. Large process computers are not available on a dedicated basis.

The interface information flow used in this project is shown in Figure 5.1.

The computer to operator communications was by means of a DEC 680 Communications System and a set of contacts. All of the output and error messages pertaining to a specific gas chromatograph were relayed by the IBM 1800 computer to the designated teletype via the communications system. The contact closure operated a light and was initiated by the monitoring software to indicate to the operator that monitoring was in progress.

The operator to computer communications link involved the use of the IBM 1800 process interrupt facility, the DEC 680 Communications System, and the card reader on the IBM 1800 computer. The process

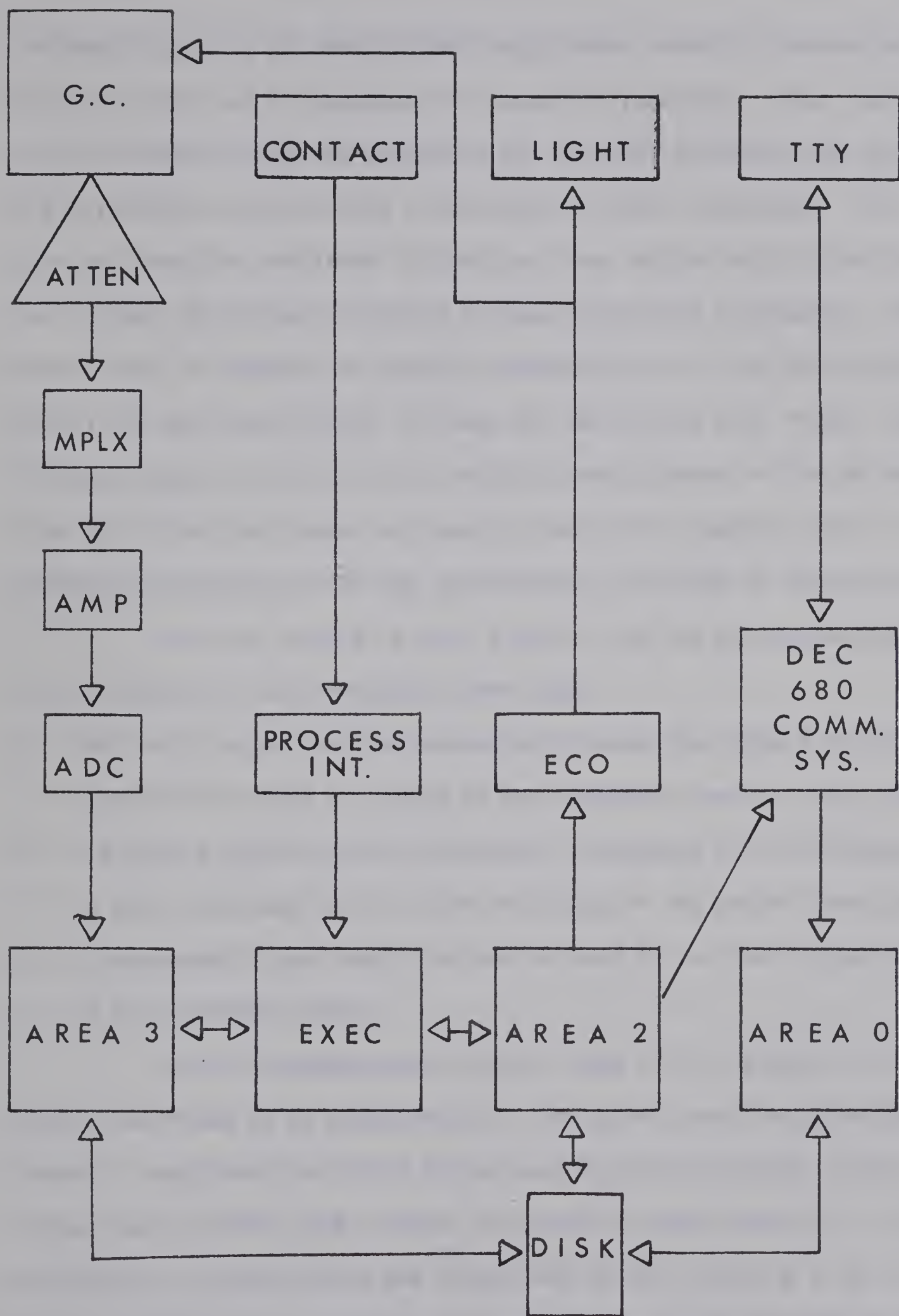


FIGURE 5-1: INFORMATION FLOW FOR G.C.-COMPUTER INTERFACE

interrupt facility of the IBM 1800 could sense contact closures and associate each set of contacts with specific functions. When the laboratory interrupt button was depressed the computer initiated the scan of the particular analog signal associated with that instrument. The software obtained the pertinent information from the job definition disk files and scanned the signal according to these specified procedures. The two other forms of operator to computer communications links involved the definition and modification of these job definition disk files. The teletype system could be used to modify certain parts of the job definition while the card reader was used to define the complete job. A further explanation of the job definition is included as Appendix E.

The wide range of analog signals from the gas chromatograph can be handled in the following three ways:

1. The analog signal can be attenuated to make the highest possible signal fall within the range of the computer's analog input point.
2. The analog signal can be selectively attenuated at the chromatograph, so that each peak falls within the range of the analog input point.
3. A programmable gain amplifier can be used to read each separate peak in an acceptable range.

For the chromatograph analysis used in this project, the first method was found to be unacceptable. The gas mixtures being analysed normally contained from 90 to 98 per cent N_2 which resulted in one very large peak (2 volts) and a number of relatively small peaks (1 - 10 millivolts). Conditioning the large peak to fall within a 0 to 20 millivolt range resulted in peaks small enough to be seriously effected by signal transmission noise. The second method was relatively simple since the gas chromatograph being used had the capability of changing

attenuations at timed intervals, as outlined in section 3.5.1 of chapter 3.

The remainder of the signal to computer link involved a multiplexer, (MPLX), an amplifier, (AMP), and an analog to digital converter (ADC). The multiplexer enabled the computer to read many different analog input points with the same ADC. The amplifier was used to boost the analog input point signals to a common range for the ADC (0 - 5 volts). This enabled the ADC to read analog input points of many different ranges. The ADC converted the analog signal to a digital number. These three devices were shared by the gas chromatograph monitoring package with the other programs on the computer requiring analog input readings.

A detailed discussion of the real-time aspects of the package with respect to the other functions of the IBM 1800 computer are beyond the scope of this thesis. The computer was operated under a partitioned core system with the main part of the gas chromatograph monitoring system core resident in a designated partition. By operating on a priority system the computer was always available to perform the chromatograph scan and required processing each time interval. Functions such as report generation were executed at a lower level of priority by a completely separate core load operating in another non-dedicated core partition. All communications between the core loads were by means of disk files. The DEC 680 Communications System enabled the report routines to execute in a matter of seconds even with a 10 character per second teletype. The report routine had to wait in the queue until its turn came for the non-dedicated partition and then quickly read the information from disk, perform a few simple calculations, and then

transfer the report to the core buffers of the PDP 8/I mini-computer associated with the communications system. The communications system was the only hardware busy during the entire 30 to 45 seconds of report printout.

5.3 Integration

Integration was carried out dynamically employing the rectangular rule. The integration section of the scan routine adjusted each area slice to the base scan rate of 16 points per second to allow for a variable scan rate.

5.4 Peak Status

The first and second derivatives of the gas chromatograph signal were used to determine the peak status. The signal of an actual peak is shown in Figure 5.2 and the two derivatives in Figures 5.3 and 5.4. The program used each digital reading received from the ADC in finite difference formulas to calculate the derivatives at each point. The derivatives then indicated peak starts, inflection points, maximums, and finishes. The logic was required to allow for new peak starts during an existing peak and missed characteristics.

A list of the possible peak statuses, their meanings, how they can be detected, and what can possibly happen next is contained in Table 5.1. Generally the program logic observes the possibility of a peak status and then confirms it by requiring that the derivatives remain within a certain range of values for a specified length of time. The range of values and the length of time are defined by the user during the job definition.

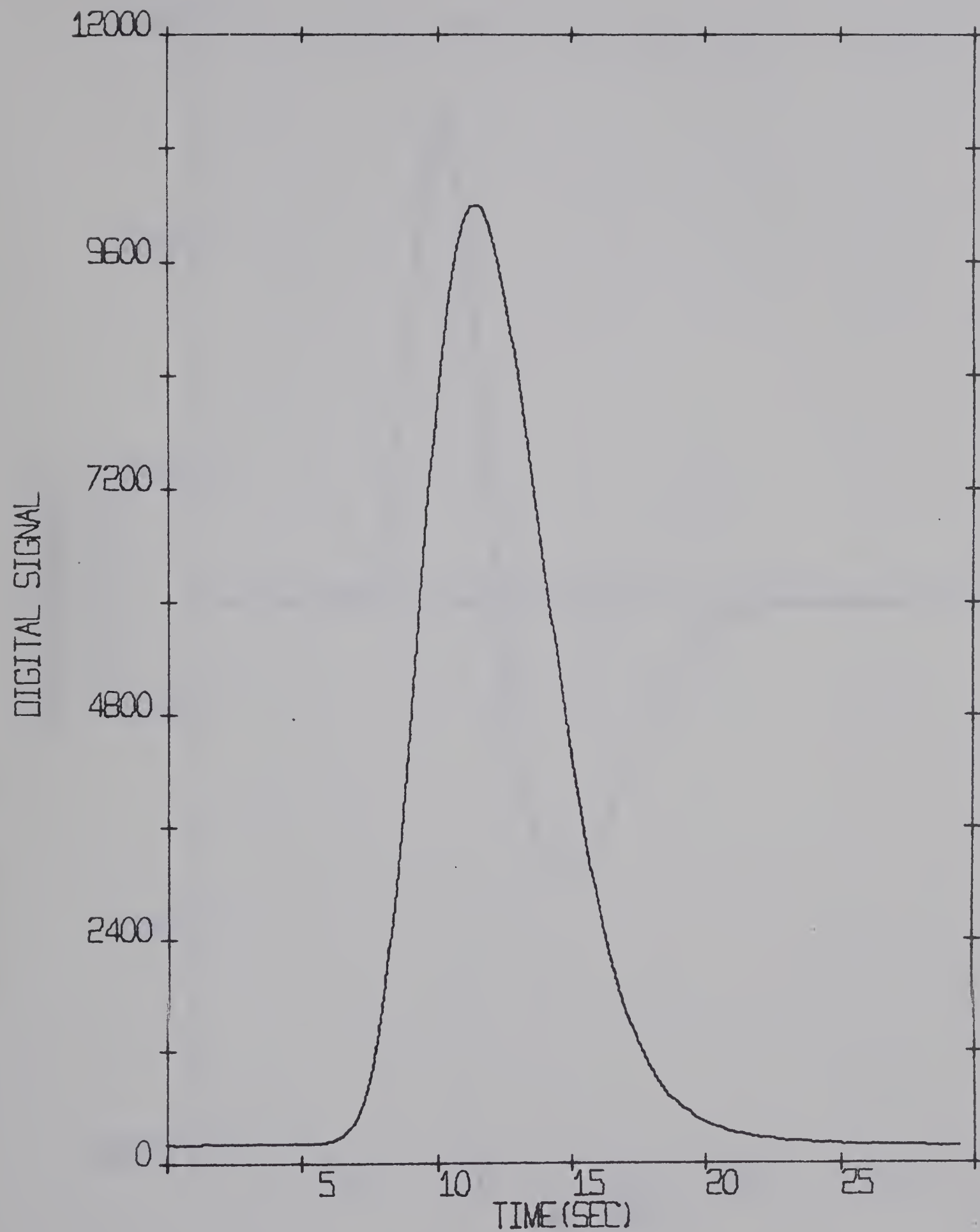


FIGURE 5-2
CHROMATOGRAPH PEAK-SIGNAL

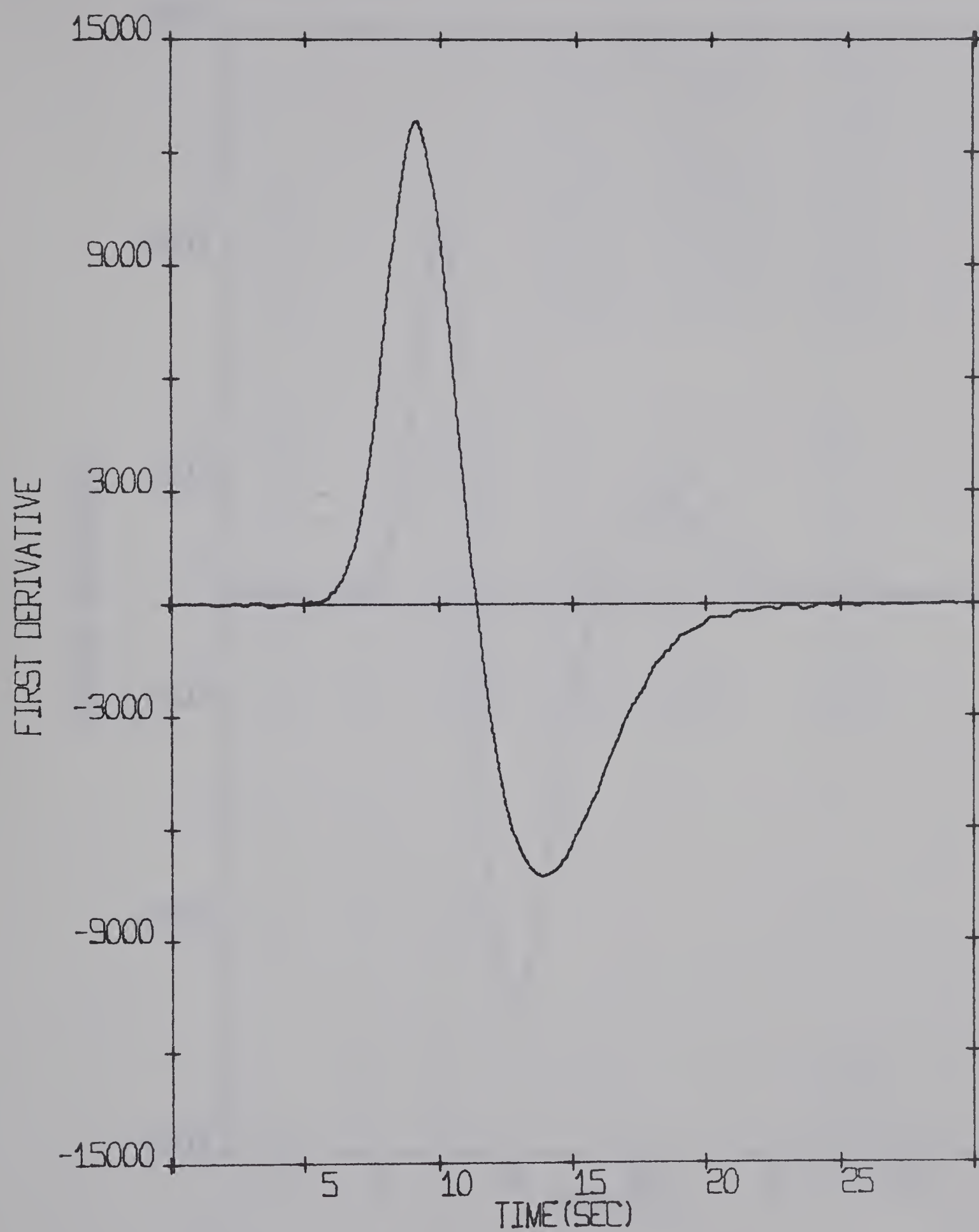


FIGURE 5-3

CHROMATOGRAPH PEAK-FIRST DERIVATIVE

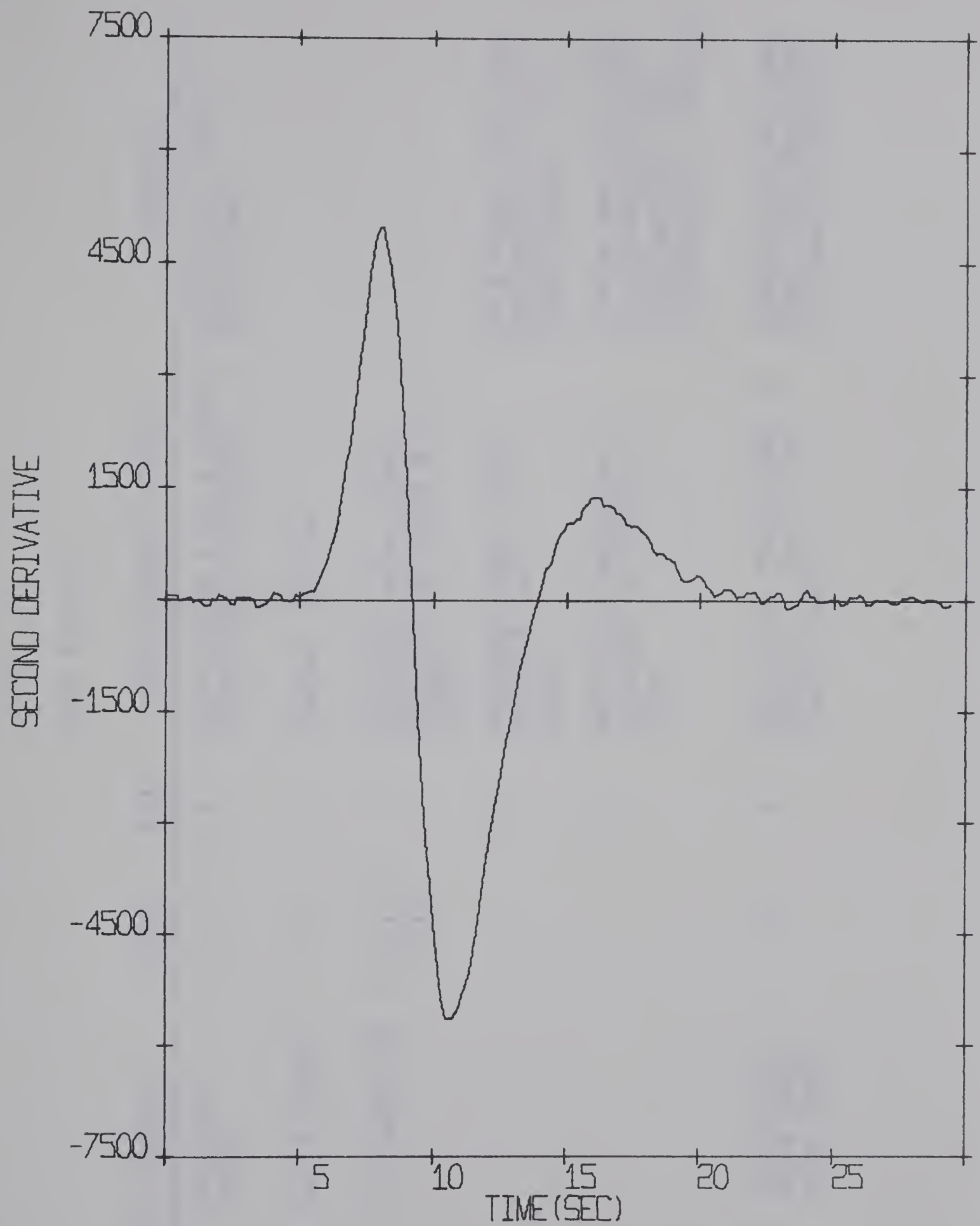


FIGURE 5-4

CHROMATOGRAPH PEAK-SECOND DERIVATIVE

TABLE 5-1

PEAK STATUS

STATUS	MEANING	ENTRY	EXIT	CONDITIONS FOR EXIT	COMMENTS
11	GC START MODE	INT	18	SUFFICIENT TIME ELAPSED TO GATHER 13 POINTS	USED FOR STARTUP OF GC ONLY
18	WAIT STATE	11	1	CONTROL ACTION	
1	ON BASELINE	18,6,12 7,10	7	POSSIBLE PEAK START DETECTED BY DER2 G.T. IHIGH	THIS PEAK TEST WAS ATTEMPTED IF DER2 TEST FAILED
			12	POSSIBLE PEAK START BY DER1 G.T. IHIGH	
			10	DROP FROM BASELINE DETECTED BY DER2 L.T. ILOW	A PEAK WAS DETECTED AND RETURNED TO THE BASELINE AND THEN SUBSEQUENTLY DROPPED
7	SUSPECTED PEAK START FROM DER2	1	2	CONFIRMED PEAK START BY DER2 G.T. IHIGH FOR IHARD COUNTS	COORDINATES OF PEAK START ARE SAVED AND INTEGRATION BEGINS

TABLE 5-1 (CONT D)

PEAK STATUS

STATUS	MEANING	ENTRY	EXIT	CONDITIONS FOR EXIT	COMMENTS
7 CONT'D					
			1	ABOVE TEST FAILS BEFORE IHARD COUNTS	NO PEAK START
12	SUSPECTED PEAK START FROM DER1	1	2	CONFIRMED PEAK START BY DER1 G.T. IHIGH FOR IHARD COUNTS	COORDINATES OF PEAK ARE SAVED AND INTEGRATION BEGINS
			1	ABOVE TEST FAILS BEFORE IHARD COUNTS	NO PEAK START
10	SUSPECTED DROP FROM THE BASELINE	1	4	CONFIRMED TO BE ON BACK OF PEAK CONCAVE DOWN BY DER2 L.T. ILOW FOR IHARD COUNTS	BASELINE RETURN WAS DETECTED (STATUS=1) THE PEAK MAY STILL BE TAILING
			1	ABOVE TEST FAILED BEFORE IHARD COUNTS	STILL ON BASELINE
2	FRONT OF PEAK	12,7,14,15	14	SUSPECTED CHANGE TO CONCAVE DOWN DETECTED BY DER2 L.T. ILOW	INFLECTION POINT ON FRONT OF PEAK

TABLE 5-1 (CONT D)

PEAK STATUS

STATUS	MEANING	ENTRY	EXIT	CONDITIONS FOR EXIT	COMMENTS
14	SUSPECTED PASSING THRU INFLECTION	2,8	3	CONFIRMED CONCAVE DOWN ON FRONT OF PEAK BY DER1 L.T. ILOW/2	BOTH DERIVATIVES ARE PASSING THRU 0
8			8	POSSIBLY AT THE PEAK MAX SINCE DER2 L.T. ILOW BUT DER1 G.T. ILOW/2	MISSED INFLECTION POINT ON FRONT OF PEAK
1			1	BOTH OF THE ABOVE TESTS FAILED	STILL ON THE FRONT OF PEAK CONCAVE UP
3	FRONT OF A PEAK CONCAVE DOWN	14,8,15	8	SUSPECTED PEAK MAX BY DER1 L.T. ILOW/2	AT MAX DER1=0 AND IS AT MAX NEG POINT
15			15	SUSPECTED NEW PEAK	FUSED PEAK ON FRONT OF ORIGINAL
8	SUSPECTED PEAK MAX	3,14,15	4	CONFIRMED TO HAVE PASSED THRU MAX BY DER1 L.T. ILOW/2 FOR ISOFT COUNTS	DER1 IS AT OR NEAR 0 AND MAX HAS BEEN ATTAINED

TABLE 5-1 (CONT D)

PEAK STATUS

STATUS MEANING	ENTRY	EXIT	CONDITIONS FOR EXIT	COMMENTS
8 CONT'D				
		14	ABOVE TEST FAILED BEFORE ISOFT COUNTS	POSSIBLE FRONT INFLECTION MISTAKEN FOR PEAK MAX
		3	HAVE NOT YET REACHED MAX SINCE DER1 L.T. ILOW/2	MAX NOT REACHED YET
4	BACK OF PEAK 8,10,16	5	CHANGE TO CONCAVE UP DETECTED BY DER2 G.T. 0 BUT APPROACHING 0 FOR IHARD COUNTS	BACK INFLECTION DETECTED TO BE HAPPENING SLOWLY
		16	SUSPECTED CHANGE TO CONCAVE UP BY DER2 G.T. IHIGH	STRONG BACK INFLECTION
15	SUSPECTED CHANGE FROM CONCAVE DOWN TO CONCAVE UP OR THE FRONT	3	NEW PEAK CONFIRMED BY DER2 G.T. IHIGH FOR IHARD COUNTS	

TABLE 5-1 (CONT D)

PEAK STATUS

STATUS	MEANING	ENTRY	EXIT	CONDITIONS FOR EXIT	COMMENTS
15 CONT'D					
			8	PEAK MAX SUSPECTED BY DER2 L.T. ILOW/2	FLATTENING OUT OF PEAK
			3	ABOVE TESTS FAILED	STILL ON THE FRONT OF PEAK CONCAVE DOWN
16	SUSPECTED CHANGE FROM CONCAVE DOWN TO CONCAVE UP ON BACK	4,17	13	SUSPECTED NEW PEAK WITHOUT RETURN TO THE WITHOUT A RETURN TO THE BASELINE DER1 G.T. IHIGH/2	BOTH DER1 AND DER2 ARE POSITIVE ON THE BACK OF A PEAK
			5	INFLECTION POINT CONFIRMED BY DER1 L.T. IHIGH/2 AND DER2 G.T. IHIGH FOR IHARD COUNTS	
			4	STILL ON BACK CONCAVE DOWN. DER1 L.T. IHIGH/2 AND DER2 G.T. IHIGH FOR ISOFT COUNTS	INFLECTION POINT NOT REACHED YET

TABLE 5-1 (CONT D)

PEAK STATUS

STATUS	WEAVING	ENTRY	EXIT	CONDITIONS FOR EXIT	COMMENTS
13	SUSPECTED NEW PEAK WITHOUT A RETURN TO BASELINE	16,5	2	NEW PEAK CONFIRMED BY DER1 G.T. IHIGH/2 FOR IHARD COUNTS	PEAK END INFORMATION AND PEAK START INFORMATION SAVED
			16 OR 5	ABOVE TEST FAILED	INFLECTION POINT APPEARED TO BE NEW PEAK. REVERTS TO ENTRY POINT
5	BACK OF PEAK PEAK CONCAVE UP	6,16,9 4	17	SHOULDER CONFIRMED	
			13	NO SHOULDER AND DER1 G.T. IHIGH/2	NEW PEAK START
			9	SUSPECTED CHANGE FROM BACK CONCAVE UP TO CONCAVE DOWN	SUSPECTED INFLECTION

TABLE 5-1 (CONT D)

PEAK STATUS

STATUS	MEANING	ENTRY	EXIT	CONDITIONS FOR EXIT	COMMENTS
5	CONT'D				
			6	SUSPECTED RETURN TO BASELINE BY DER1 L.T. ILOW AND DER2 L.T. ILOW	
9	SUSPECTED CHANGE FROM BACK CONCAVE UP TO CONCAVE DOWN	6, 2	17	BACK OF SHOULDER PEAK INDICATED BY DER2 L.T. ILOW FOR IHARD COUNTS	
			5 OR 6	SHOULDER TEST FAILED	REVERTS TO ENTRY POINT
17	SHOULDER	9	16	CHANGE FROM CONCAVE DOWN TO CONCAVE UP BY DER2 G.T. IHIGH	SHOULDER HAS ENDED
6	SUSPECTED RETURN TO BASELINE	5	1	RETURN CONFIRMED IF DER2 G.T. ILOW AND DER1 WAS IN THE DEADBAND FOR IHARD COUNTS	

TABLE 5-1 (CONT D)

PEAK STATUS

STATUS	MEANING	ENTRY	EXIT	CONDITIONS FOR EXIT	COMMENTS
6	CONT'D				
9				BASELINE TEST FAILED BECAUSE DER2 L.T. ILOW	INFLECTION MISTAKEN FOR RETURN TO BASELINE
5				BASELINE TEST FAILED IF DER1 FALLS OUT OF THE DEADBAND BEFORE IHARD COUNTS	TAIL MISTAKEN FOR RETURN TO THE BASELINE
19	END OF RUN			CONTROL ACTION	

The calculation of the derivatives were carried out using a least-squares technique outlined by Savitzky and Golay (43). The first derivative at the central point of a 13 point string was calculated according to the following formula

$$c_1(dy/dx)_7 = 3(Y(10) - Y(4)) + 2(Y(9) - Y(5)) + (Y(8) - Y(6)) \quad (5.1)$$

where:

$$c_1 = 28 h$$

$$h = \text{interval length}$$

Rather than use (dy/dx) the value of $c_1(dy/dx)$ was used to avoid the unnecessary repetitive division. The second derivative was calculated using a simple difference between the first derivatives at the 10th and the 4th points, as follows:

$$c_2(d^2y/dx^2) = c_1(dy/dx)_{10} - c_1(dy/dx)_4 \quad (5.2)$$

where:

$$c_2 = 168 h^2$$

5.5 Baseline

A new baseline was determined each time that the peak status indicated a return to the baseline had occurred. This is illustrated in Figure 5.5. The first two groups of peaks caused baselines to be drawn as straight lines connecting peak start and peak finish points (AB and CD). The third group of peaks was complicated by a detected drop below the baseline at point F. This group was divided into two subgroups; the first with baseline EF, and the second with baseline FG. The area below the baseline was calculated as a trapezoidal area

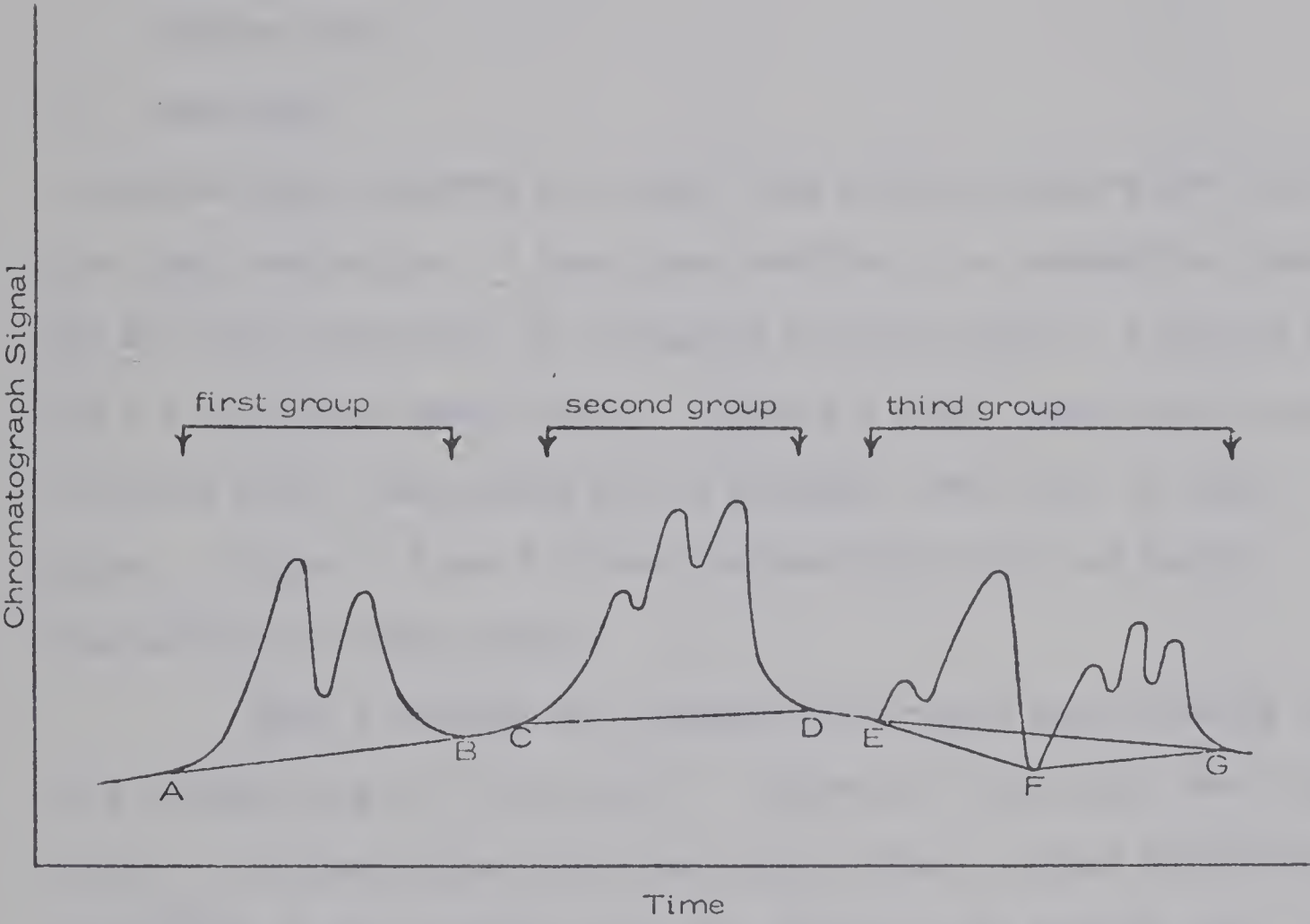


FIGURE 5-5: BASELINE CALCULATIONS

bounded by the initial and final baseline points, and the electronic zero baseline.

5.6 Separation of Unresolved Peaks

The scan logic recognized the following two categories of unresolved peaks.

1. shoulder peaks
2. fused peaks

A shoulder peak occurred on a major peak without changing the sign of the first derivative. A fused peak resulted in an unexpected change in the first derivative to increasing positive values. Figures 5.6 to 5.8 illustrate these points. Figure 5.5 shows three sets of peaks, a normal peak, a major peak with a shoulder, and a pair of fused peaks. Figures 5.7 and 5.8 show the resulting first and second derivatives for these peaks.

When a shoulder was detected the program began looking for the shoulder end or "slice point". Figure 5.9 illustrates the "slice-point". The point where $\Delta Y/\Delta X$ was greater than or equal to the first derivative at the shoulder start was chosen as the shoulder end. The area above the line joining the shoulder start and shoulder end was assigned to the minor component.

When a group of fused peaks were detected the total area was divided into the component areas according to which of four optional ways was chosen at job definition. The calculation methods can be explained with reference to Figure 5.10. A type 4 calculation therefore causes the fused peaks to be treated as a major peak and a shoulder. Calculation types 2 and 3 ignore areas which should obviously be included in the analysis.

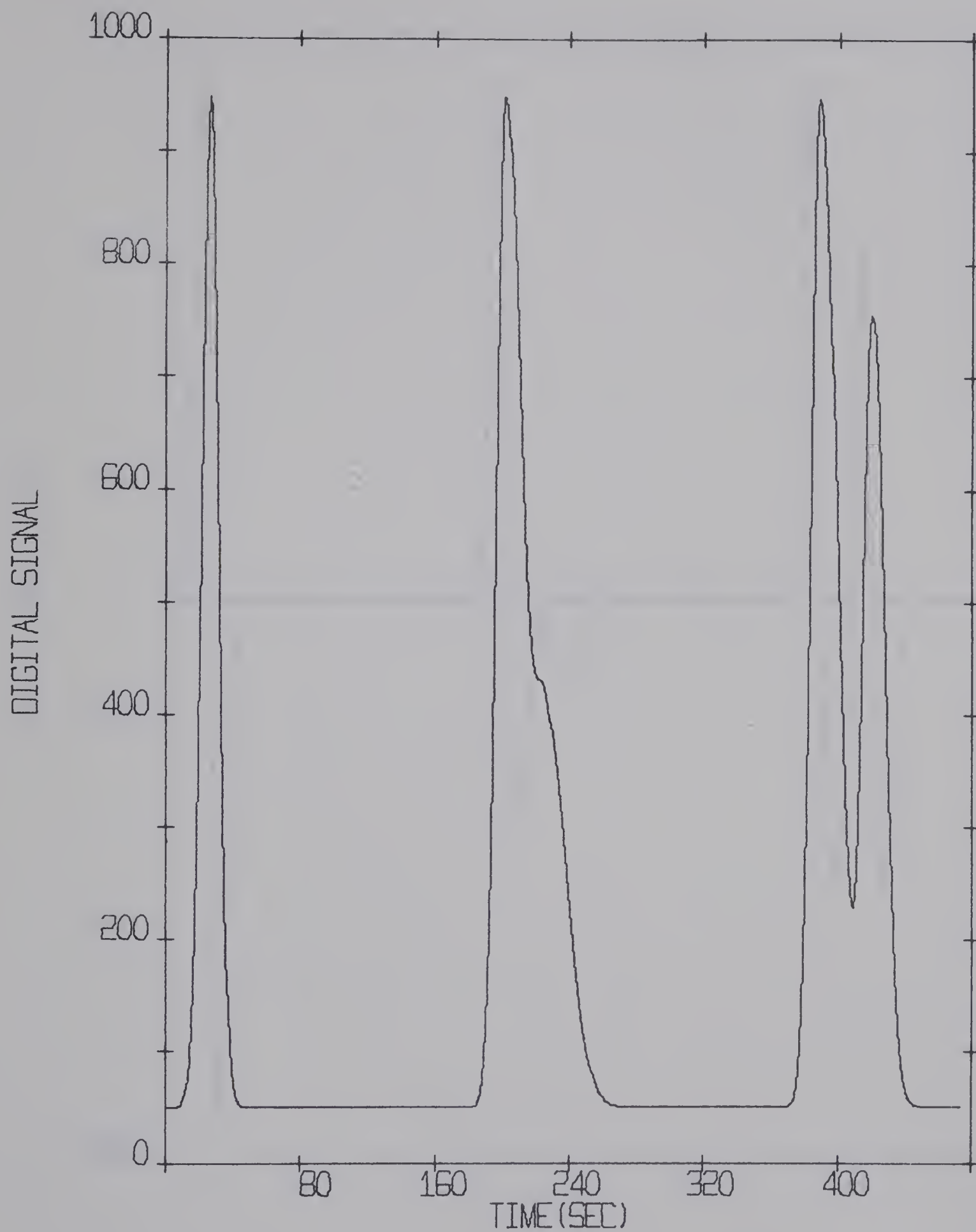


FIGURE 5-6

NORMAL, SHOULDERED, AND FUSED PEAK SIGNALS

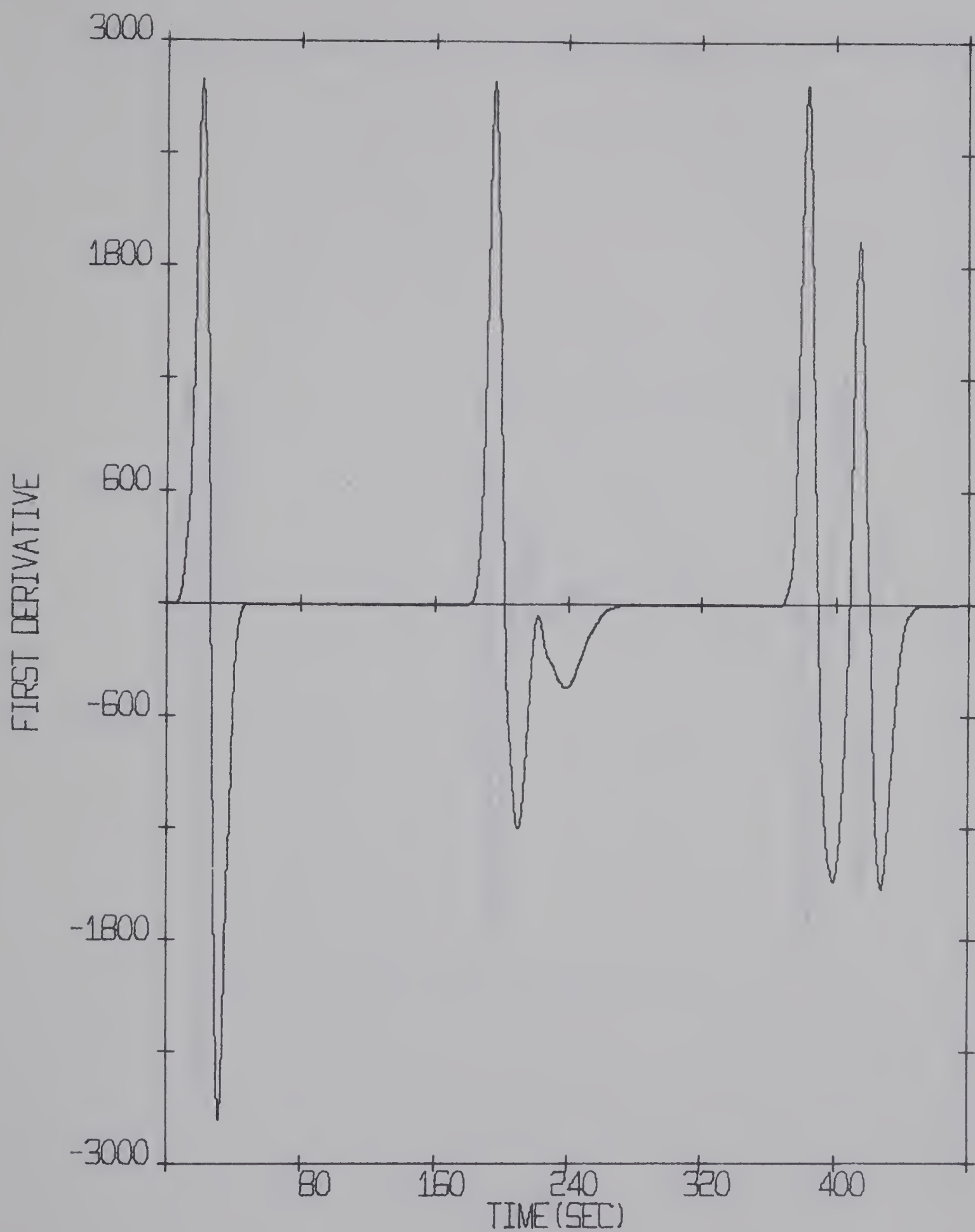


FIGURE 5-7

NORMAL, SHOULDERED, AND FUSED PEAK FIRST DERIVATIVE

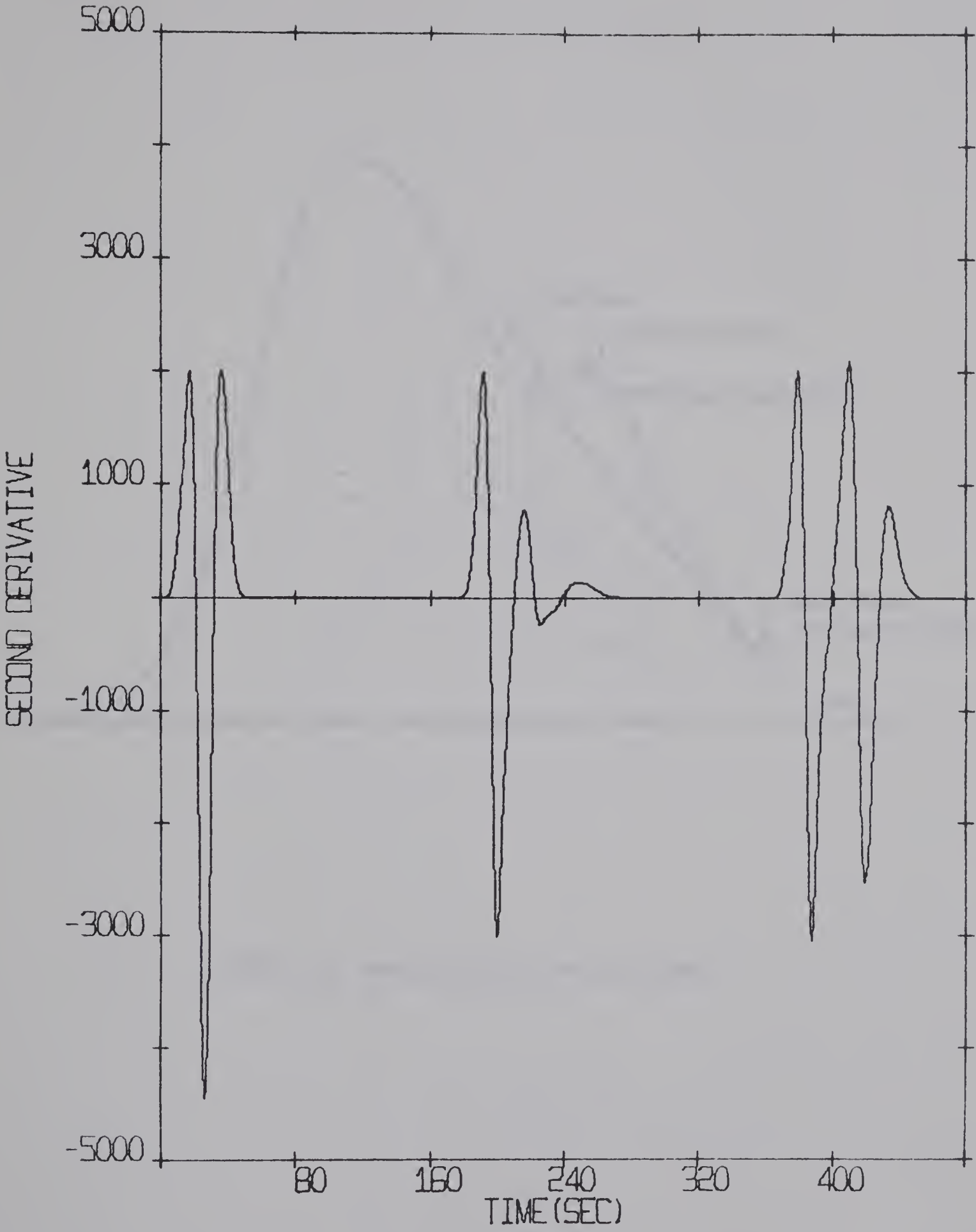


FIGURE 5-8
NORMAL, SHOULDERED, AND FUSED PEAKS SECOND DERIVATIVES

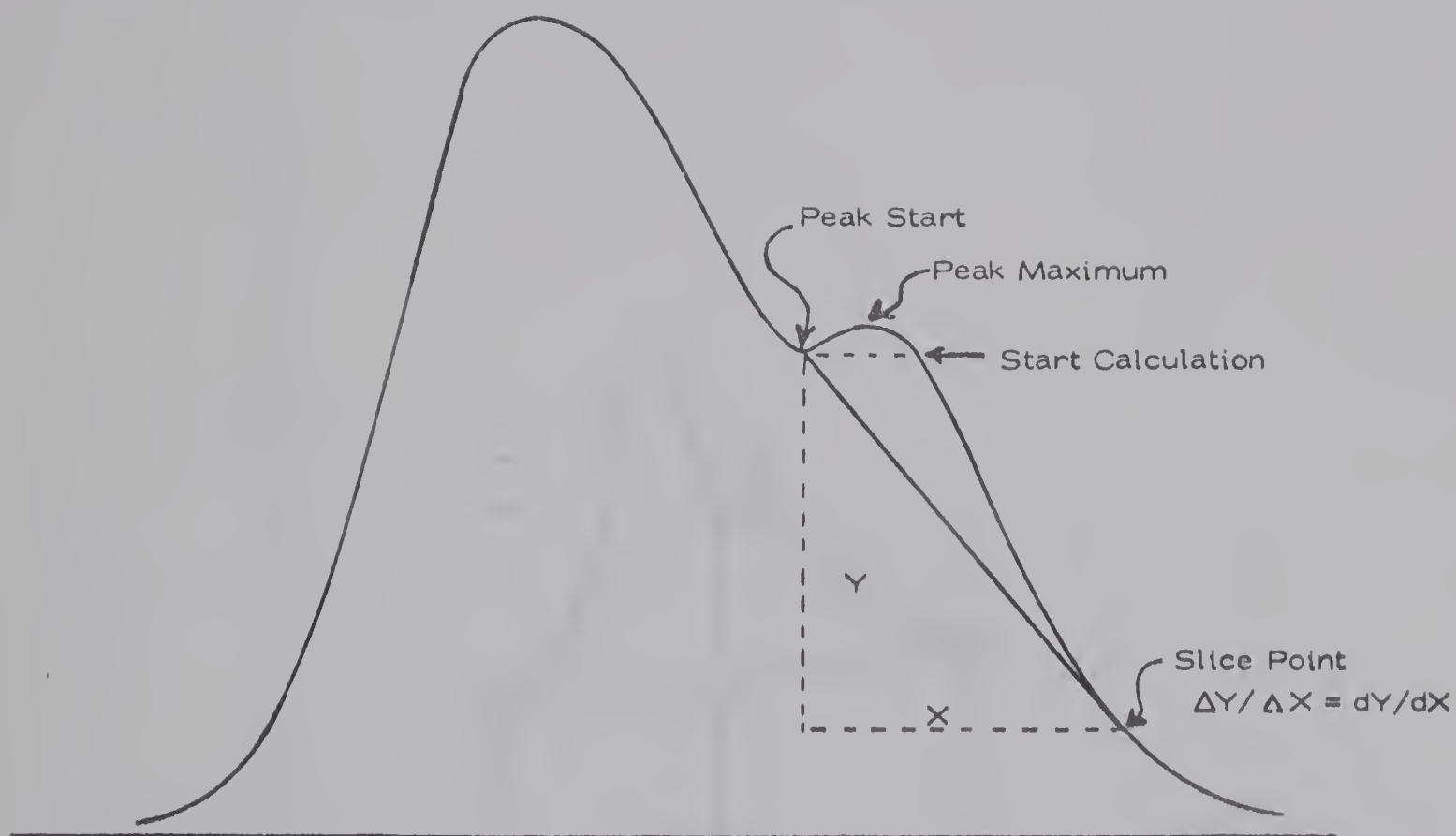


FIGURE 5-9: SHOULDER AREA CALCULATIONS

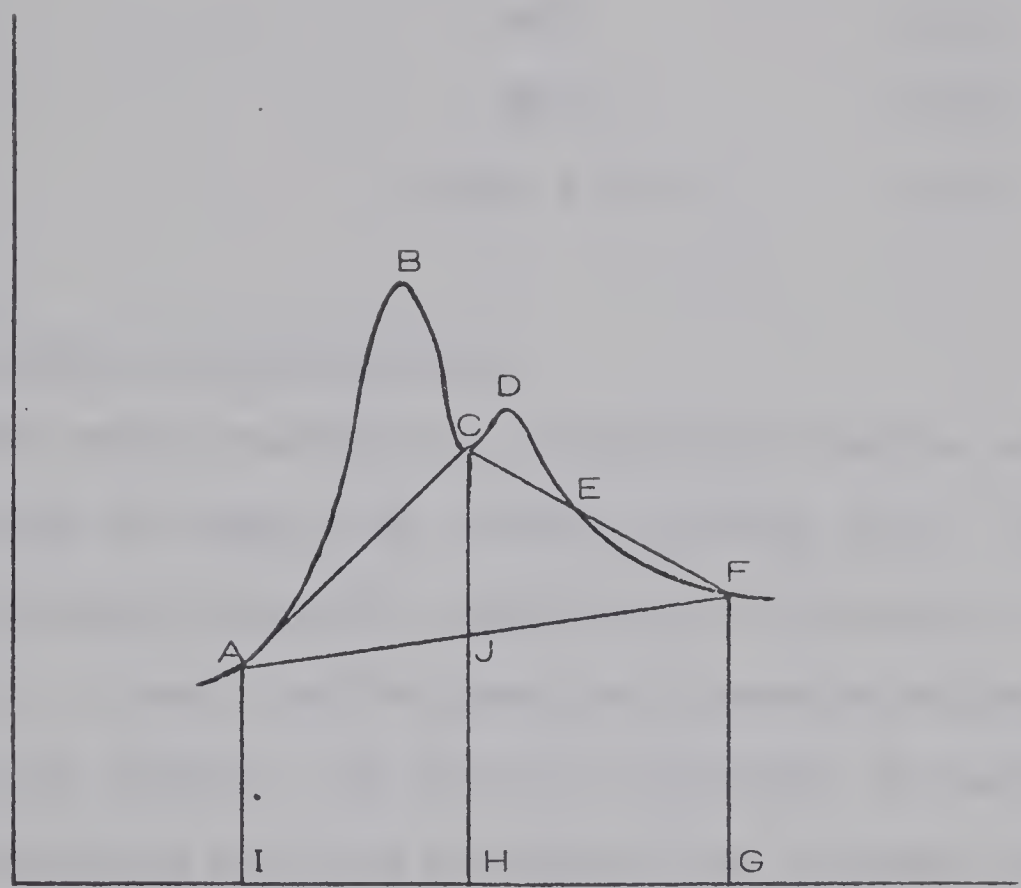


FIGURE 5-10: FUSED PEAK AREA ALLOCATION

TABLE 5.2
AREA ASSIGNMENT OF FUSED PEAKS

TYPE	FIRST PEAK AREA	SECOND PEAK AREA
1	ABCJA	CDEFJC
2	ABCA	CDFC
3	ABCJA	CDFC
4	ABCJA + CFJC	CDFC

5.7 Precautions in Peak Resolving

The method of dropping a perpendicular from the valley of two fused peaks was shown to be in error by Kaiser (29). The errors that are encountered using this procedure are illustrated in Figure 5.11. A pair of poorly resolved peaks were generated mathematically from a Gaussian formula. The solid line represents the additive area, that is the observed area, and the dotted lines represent the true component peaks. Dropping a perpendicular resulted in peak 1 losing area A and gaining area B. Peak 2 lost area D and gained C. As can be observed in Figure 5.11 these areas are not equal. As changes in chromatograph conditions bring about slight changes in the peak shapes the relative sizes of these areas will change. For unresolved peaks changes in peak shapes will have a much larger effect on area reproducibility than it will for completely resolved peaks. Also the relative sizes of these exchanged areas will change with the relative sizes of the two peaks. This would tend to make a non-linear calibration curve requiring more calibration data than a linear calibration curve.

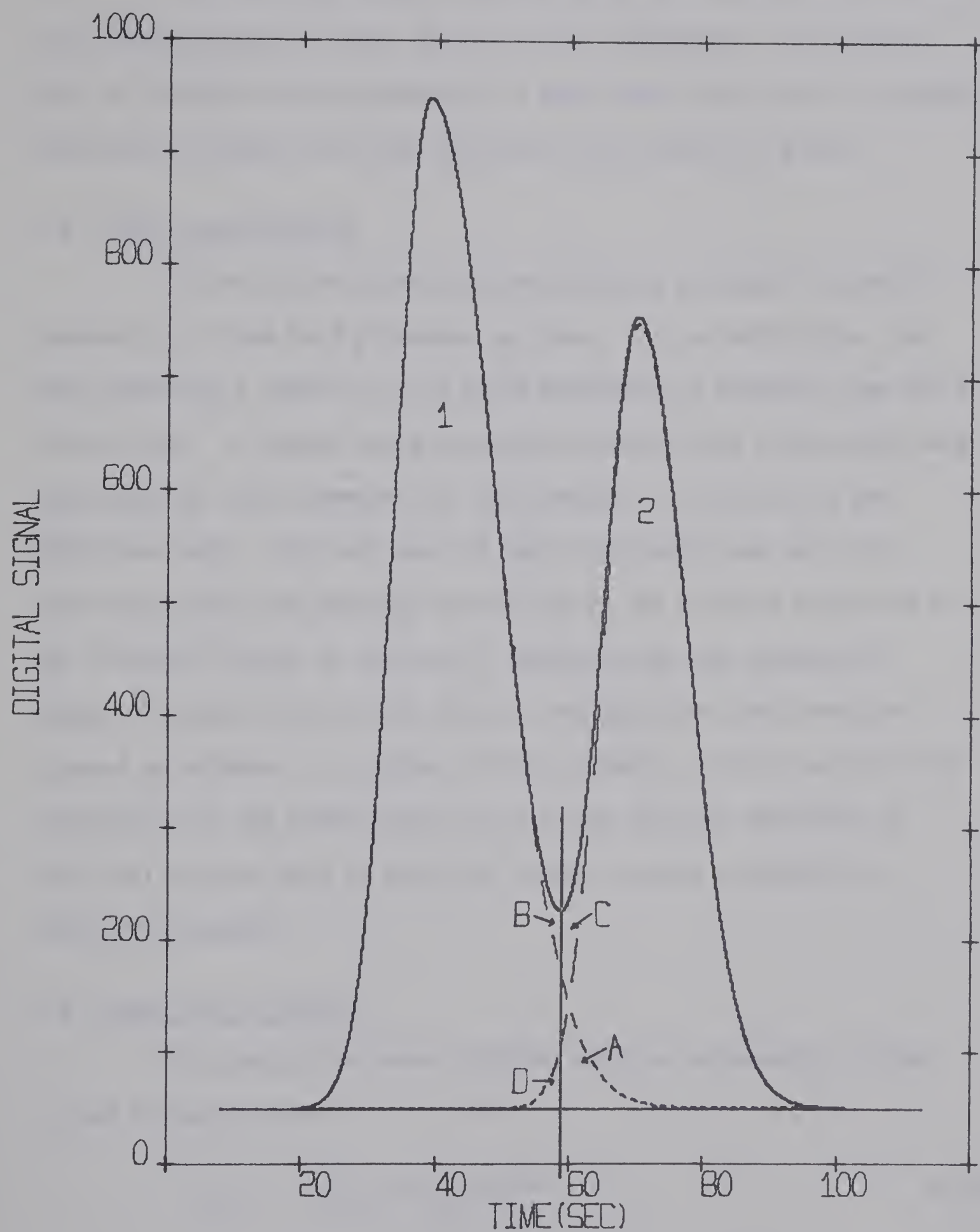


FIGURE 5-11

AREA ALLOCATION ERRORS WITH FUSED PEAKS

Figure 5.12 depicts a possible error that could result from a misinterpretation of what appears to be a shoulder. The additive area of two major peaks appeared as a major peak with a small shoulder. The areas assigned to the two peaks would be grossly in error.

5.8 Peak Identification

If the job required that the peaks be assigned to specific components, a time band procedure was used. At job definition, the user specified a number of time bands defined by a starting time and a finish time. All peaks whose maximum occurred within a time band were considered as that component for the purposes of calculating the normalized area. The peak area of each individual peak was still reported so that the operator could observe the relative magnitude of the individual peaks or for use in recalculating the normalized areas. Any peaks not falling into an assigned time band were considered as unknowns. The areas of the unknowns were not used for the calculation of the normalized area, but the relative magnitude of the total unknown area to the total known area was reported for reference purposes.

5.9 Noise and Filtering

The derivatives were filtered using an exponential filter in the following form:

$$dy_i' = (dy_i + dy_{i-1}')/2^{EXP} \quad (5.3a)$$

where dy_i' = filtered value at the i^{th} point
 dy_i = raw value at the i^{th} point
 EXP = filter factor

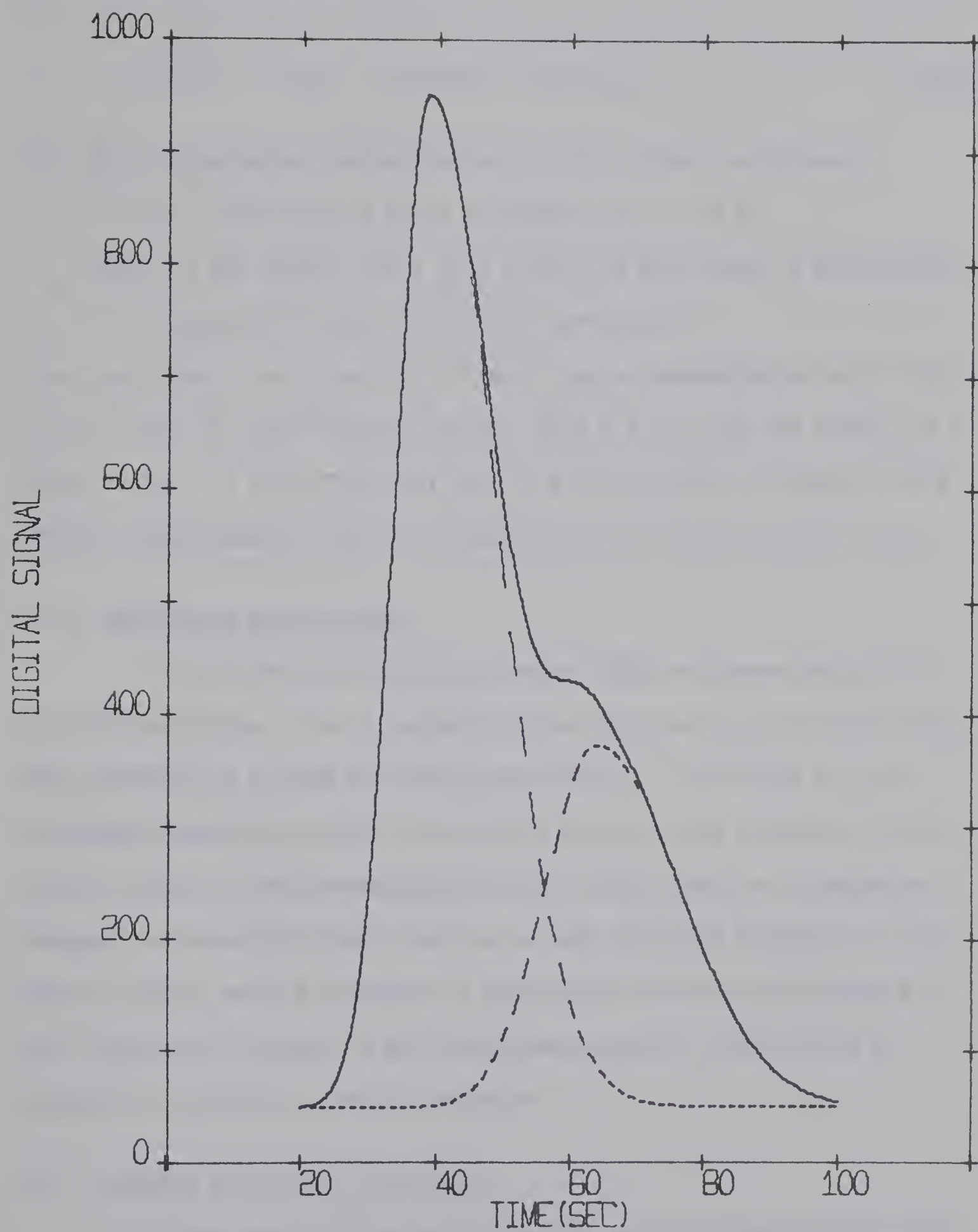


FIGURE 5-12

TWO MAJOR PEAKS APPEARING AS A SHOULDERED PEAK

This can be rewritten as follows:

$$2^{(\text{EXP} - 1)} dy_i' = 0.5 dy_i + 0.5 dy_i' \quad (5.3b)$$

This form illustrates the weaknesses of this filter as follows:

1. The true filter factor has a constant value of 0.5.
2. Values of EXP other than 1 only alter the magnitude of derivatives.
3. It is impossible to not filter the derivatives.

Tests reported in section 13.1 of this chapter demonstrate that filter factors must be significantly smaller than 0.5 to have any effect as a noise filter. A description of possible alternatives to replace this totally unacceptable filter is presented in this later section also.

5.10 Resolution and Accuracy

The analog to digital converter (ADC) was operated with 14 bits of resolution. For a typical analog input point of 20 millivolts this resulted in 0.0006 millivolts resolution. The effect of this increased resolution on the integration accuracy was reduced by noise and by errors of the chromatograph system other than the integration. Baumann and Brown (3) found that for a well designed electronic integrator system, only 5 per cent of the total error was attributable to the integration system. A well designed computer system would be expected to exhibit a similar behavior.

5.11 Summary of Valuable Features

There are eight valuable features which helped to make this program package acceptable:

1. Variable scan rate.

As far as making the package applicable to general analyses

this was the foremost feature. Without this feature an analysis with a variety of peak widths became impossible to do with any accuracy. Scan rates of 16, 8, 4, 2, and 1 points per second; and 1 point every 2 or 4 seconds were available.

2. Dynamic operation

The calculation of derivatives and areas in a dynamic fashion made it possible to operate the system with a minimum storage requirement. A process computer shared between as many different functions as this one, typically suffers from a shortage of time available to transfer large amounts of data to disk files. (A dedicated gas chromatograph computer can function very well on a data storage basis, particularly if some reduction of points occurs before storage on disk.)

3. Dynamic baseline

The baseline was determined each time that the derivatives indicated a straight line occurred for a specified length of time. This compensated for normal baseline drifts.

4. Variable report routine

At the end of a run a report was produced on the designated teletype. The information available in the report was tailored to the needs of each user. The following basic information was available:

- a. raw peak areas
- b. corrected peak areas (raw peak area - base area)
- c. coordinates of peak starts and finishes
- d. coordinates of peak maximums
- e. coordinates of shoulder starts and finishes

Normally the report would contain the corrected peak areas, the percentages of total area, elution time, and alphanumeric name of each peak.

As well, the percentages of total areas could be adjusted to account for component response factors. Each report generally included certain header information such as date, time, chromatograph number, and the job definition number that was used. Since the report generation was carried out by a separate coreload coded in Fortran, new types of reports can be included easily.

5. Operation as a core resident coreload

By operating under a partitioned core system it was possible to maintain a core resident program. This generally resulted in a near instant response to the closing of the interrupt contacts and data acquisition at every specified interval.

6. Ability to operate electrical contacts

The ability to open and close contacts made it possible for the computer to supervise analyses as well as monitor them. During this research program a hardware device on the chromatograph was employed to supervise the continuous analysis cycle. A transition to computer control would be a simple matter; eliminating the need for the extra hardware required for each gas chromatograph.

7. Simple job definition

The two simple job definition steps have been described in detail in Appendix E. Once the values for the scan parameters were selected as outlined in section 5.12, the job definition could be completed without any computer programming knowledge.

8. Use of the DEC 680 Communications System and partitioned core for report generation

The report was generated immediately after a scan was completed. In order to insure that the report generation on slow output

teletypes from a multi-chromatograph system does not hinder the turn around time this type of a system was required.

5.12 Selection of Scan Parameters

In order to define a job the analyst was required to specify values for seven scan parameters. In order to aid users in choosing the values of these parameters, a Fortran program was written which calculated the derivatives at each point for a stored chromatogram. By surveying the values and behavior of the derivatives the scan parameters could be chosen. The program, TEST, is documented in Appendix F.

The Gas Chromatograph Monitoring Package was modified so that the user was able to store a chromatograph scan rather than process it dynamically in the usual manner. When this special option was specified the program package sampled the chromatogram at a scan rate of 16 points per second and stored the data in a disk file. During this special short term status all other chromatographs were locked out of the system. Once the data accumulation was complete the system was returned to a normal status.

The data was now available to the off-line program TEST. This program calculated the derivative values at each point. By operating at different scan rates the fastest scan rate which still resulted in normal first and second derivatives could be found. Then the data at this optimum scan rate could be surveyed to choose corresponding values of IHIGH, ILOW, IHARD and ISOFT without difficulty. As demonstrated in section 5.9 the values of IEXP1 and IEXP2 had no effect on the job except to multiply the derivative values by constants. Therefore,

TABLE 5.3
SCAN PARAMETERS

PARAMETER NAME	PURPOSE
ISCAN	determine scan rate by the formula: $pps = 16/2 ** ISCAN$
IHIGH	upper limit of deadband around derivatives
ILOW	lower limit of deadband around derivatives
IHARD	counts required to confirm certain suspected statuses
ISOFT	counts required to confirm all other suspected statuses
IEXP1	first derivative filter constant
IEXP2	second derivative filter constant

advisable values for them would be 1. A few general rules for the scan parameters were as follows:

1. The scan rate was as high as was possible without hindering peak detection due to noise propagation to the derivatives.
2. IHIGH was generally in the range 10 to 30. ILOW usually was specified as -IHIGH.
3. The value of IHARD was generally best specified by referring to the data generated by the off-line program.
4. ISOFT was generally chosen to be only slightly less than IHARD.

Generally only two types of peaks complicated the parameter picking. The first of these were extremely slow peaks. The derivatives of these peaks were of comparable size to the baseline noise and were not reliable for making decisions, particularly the peak finish. This problem was rectified for all peaks encountered by including scan rates of 1 point every 2 seconds and 1 point every 4 seconds. The second class of peaks involved extreme tailing. Again it became difficult to observe the true peak finish due to the noise effect. By specifying an IHIGH value slightly above the fluctuations caused by the noise and an IHARD value large enough to force the peak finish to be delayed sufficiently, a peak finish can be detected. However, as with all gas chromatograph methods the best results were obtained when severe tailing was eliminated by good analysis design.

The optimum value of the scan rate was influenced by two conflicting factors. For fast scan rates the magnitude of the second derivative was equal to, or exceeded by, the noise propagated from the raw signal. This resulted in a complete masking of the second derivative by the noise. Scan rates slower than the optimum caused the

thirteen points used in the derivative calculation to become too widely spaced. For proper results the thirteen points should only include one inflection point or maximum at a time (43). The first point is demonstrated in Figures 5.13 and 5.14. Both of these plots are of the same chromatographic peak, H_2O ; the derivatives in Figure 5.13 were calculated from a scan of 1 point per second, and the derivatives in Figure 5.14 from a scan of 2 points per second. The second derivative at the lower scan rate exhibits the proper characteristics for a chromatographic peak. The second derivative at the higher scan rate does not. The second derivative has been partially masked by noise which was propagated from the raw chromatographic signal. As well, faster scan rates provide better integration accuracy and reduce the error in locating peak maximums.

5.13 Modifications

5.13.1 Noise and Filtering

An ultimate digital filter would enable the programs to detect all peaks using the maximum scan rate. Since the digital filters included in the package were inadequate and lacked flexibility, various other common digital filters were tested. Two separate methods were tested, filtering the signal, and filtering the calculated derivatives. Failing to obtain the necessary derivatives to justify a single scan rate package, the ability of various filters to allow scan rates slightly above the optimum were tested. The testing was carried out on actual chromatograph data through the RAWLD plotting facility documented in Appendix F. A plot of the unfiltered peak is given in

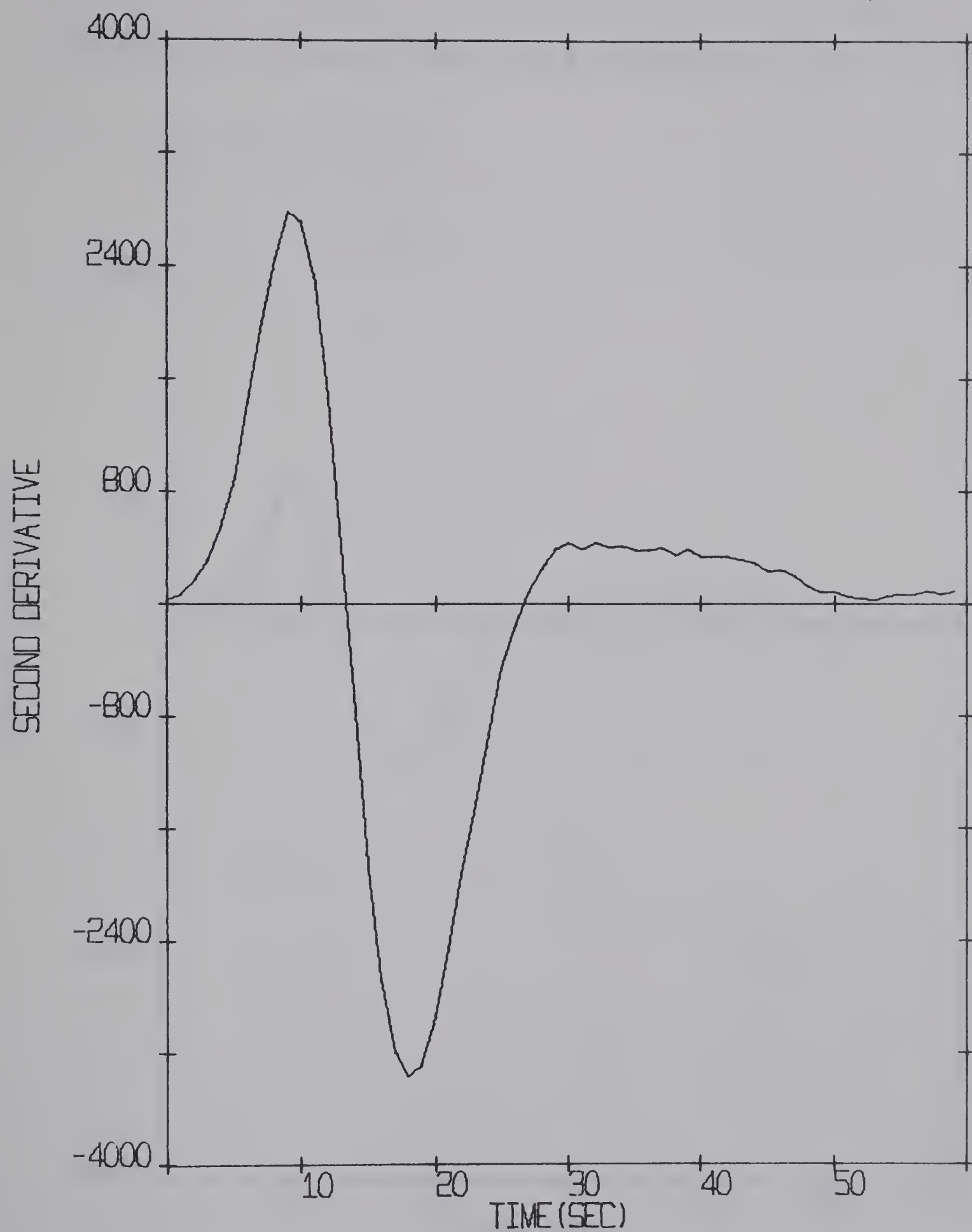


FIGURE 5-13

H₂O PEAK AT 1 PPS.

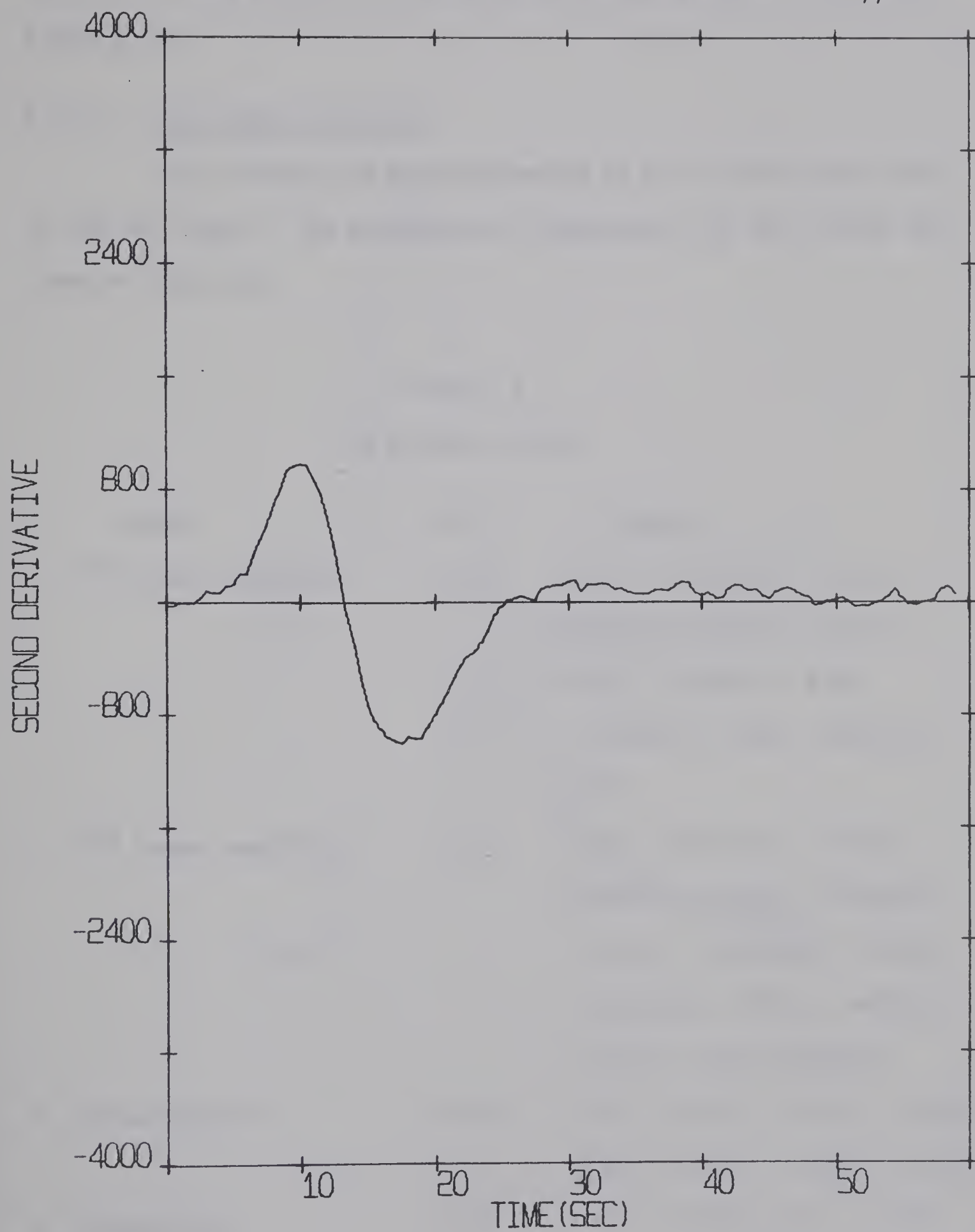


FIGURE 5-14

H₂O PEAK AT 2 PPS.

Figure 5.15 and a plot of the resulting first derivative is given in Figure 5.16.

5.13.1.1 Raw Signal Filtering

Four filters and one combination of two filters were tried on the raw signal. The mathematical formulations for the filters are given in Table 5.4.

TABLE 5.4
RAW SIGNAL FILTERS

NAME	REF.	FORMULA
1. 3 rd Order Smoothing	(43)	$Y(7) = [-11(Y(1) + Y(13)) + 9(Y(3) + Y(11)) + 16(Y(4) + Y(10)) + 2(Y(5) + Y(9)) + 24(Y(6) + Y(8)) + 25y(7)] / 143$
2. 5 th Order Smoothing	(43)	$Y(7) = [110(Y(1) + Y(13)) - 198(Y(2) + Y(12)) - 160(Y(3) + Y(11)) + 110(Y(4) + Y(10)) + 390(Y(5) + Y(9)) + 600(Y(6) + Y(8)) + 677 Y(7)] / 2431$
3. Spike Removal	(27)	$Y(12) < Y(13) \quad \text{if } Y(11) < Y(13)$ $Y(12) > Y(13) \quad \text{if } Y(11) > Y(13)$
4. Exponential	(12)	$Y(7) = \alpha Y(7) + (1 - \alpha) Y(6)$
5. Combination		1. & 3.

The results are shown in Figure 5.17. The best results were obtained with an exponential filter with a factor (α) of 0.10. This

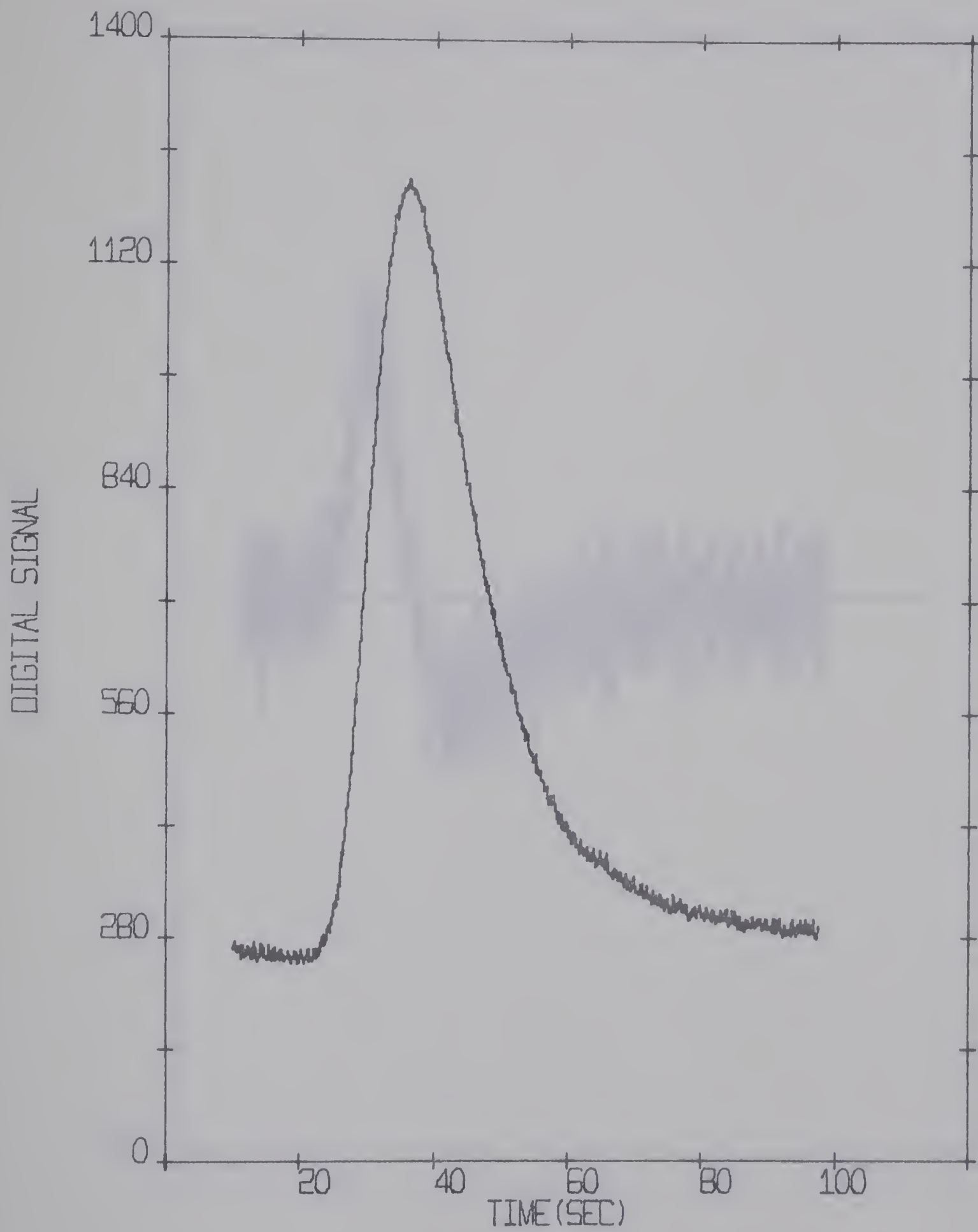


FIGURE 5-15
UNFILTERED SIGNAL

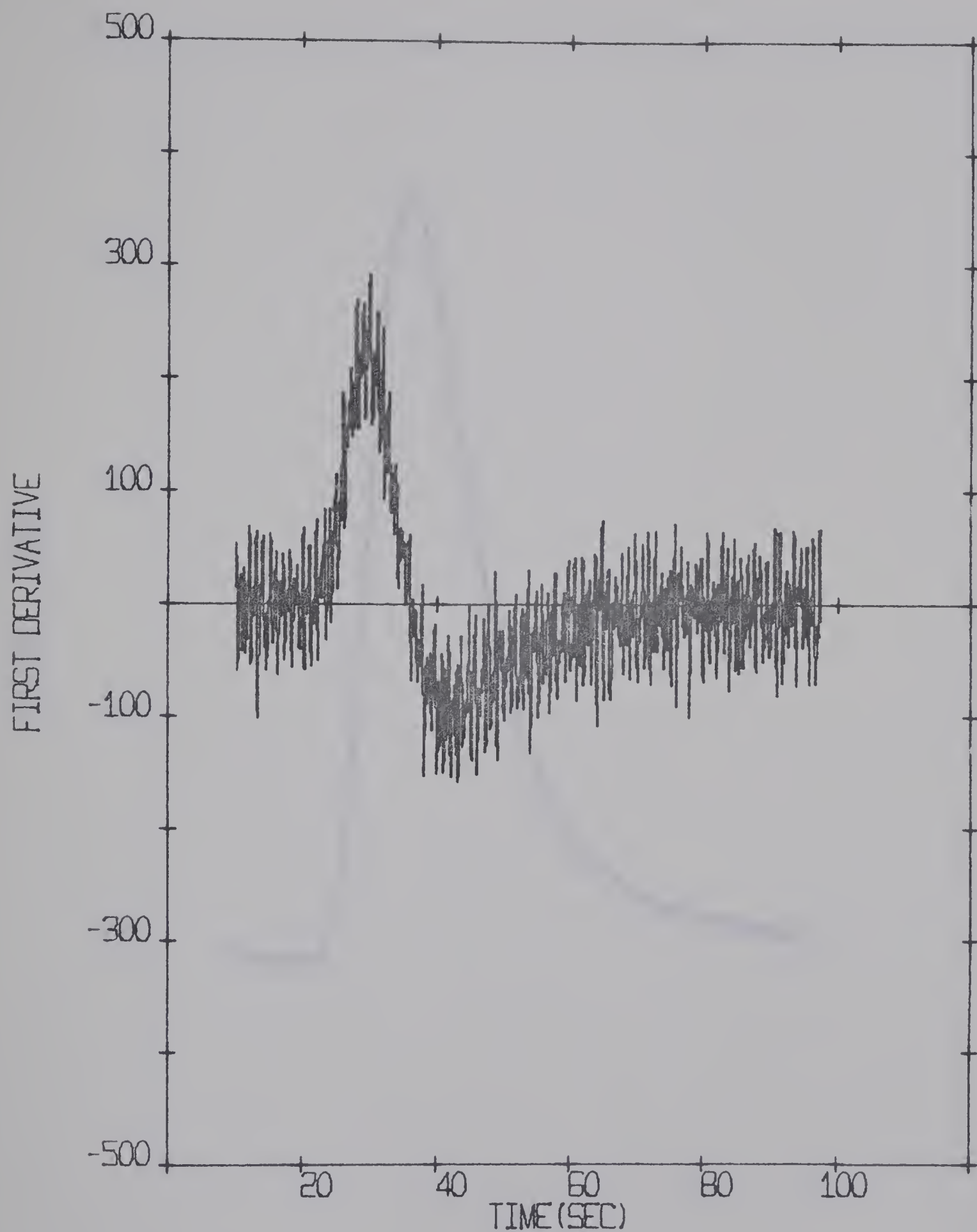


FIGURE 5-16

UNFILTERED FIRST DERIVATIVE (16 PPS)

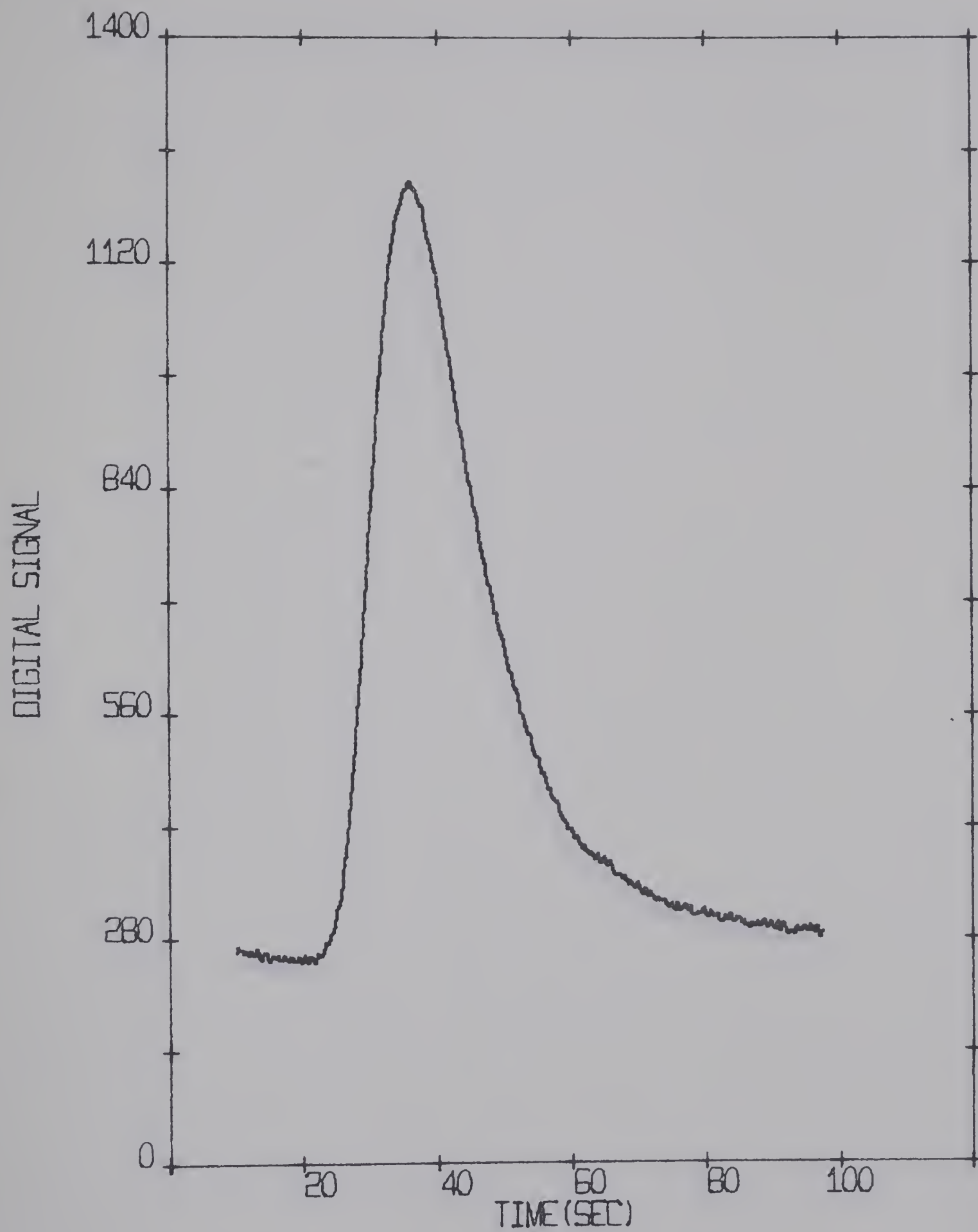


FIGURE 5-17 A
13 POINT 3 RD ORDER FILTER

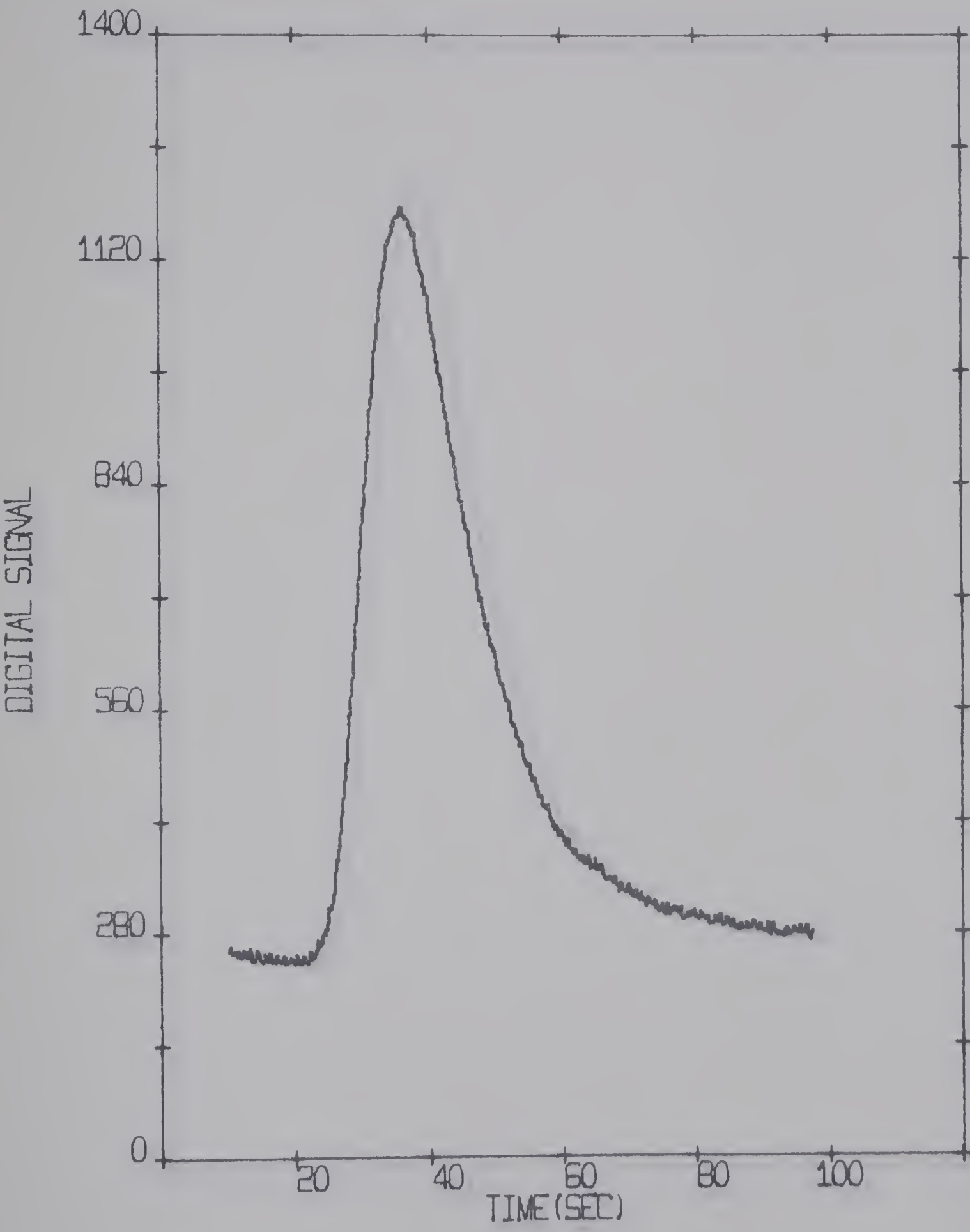


FIGURE 5-17 B
13 POINT 5 TH ORDER FILTER

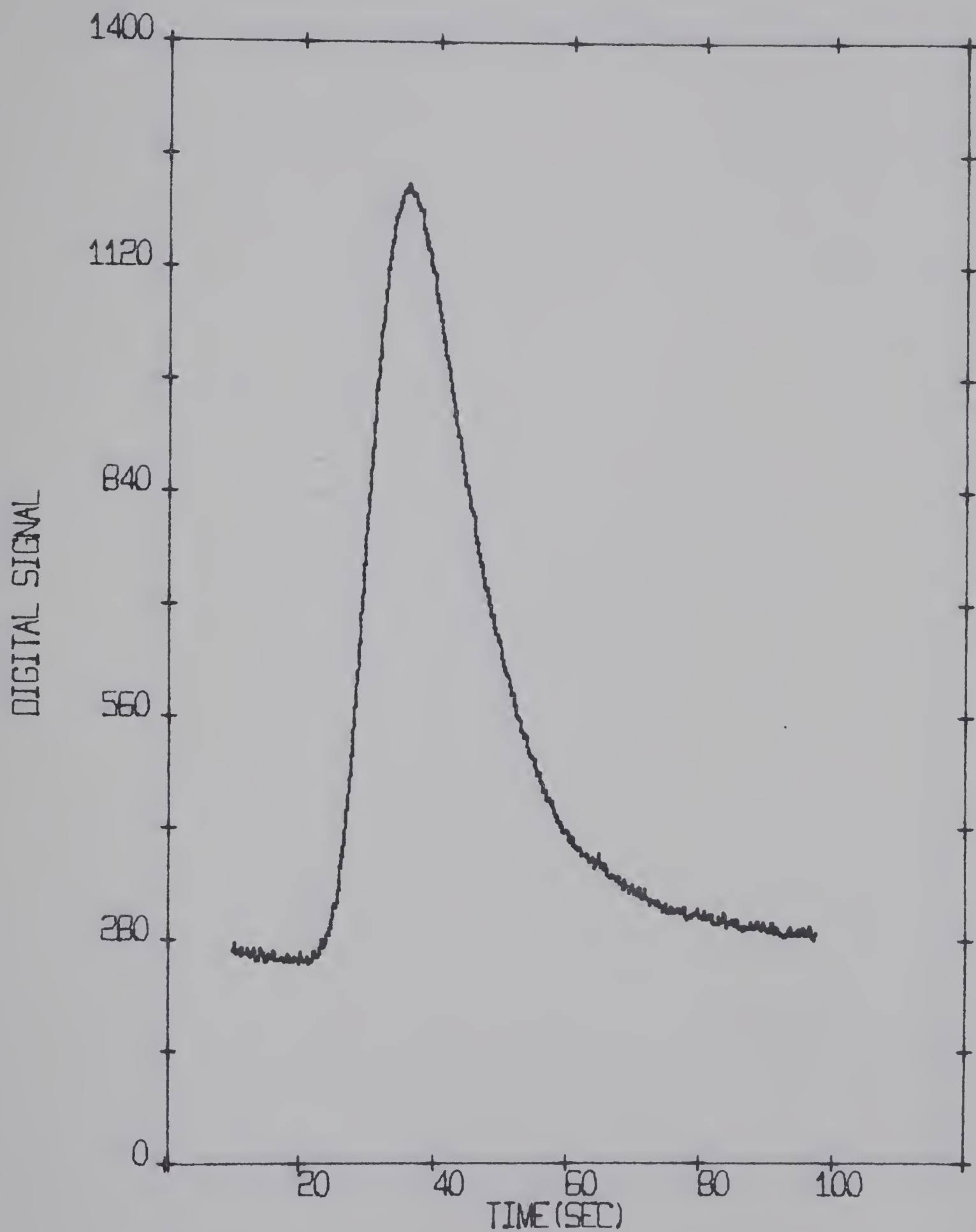


FIGURE 5-17 C
SPIKE REMOVAL FILTER

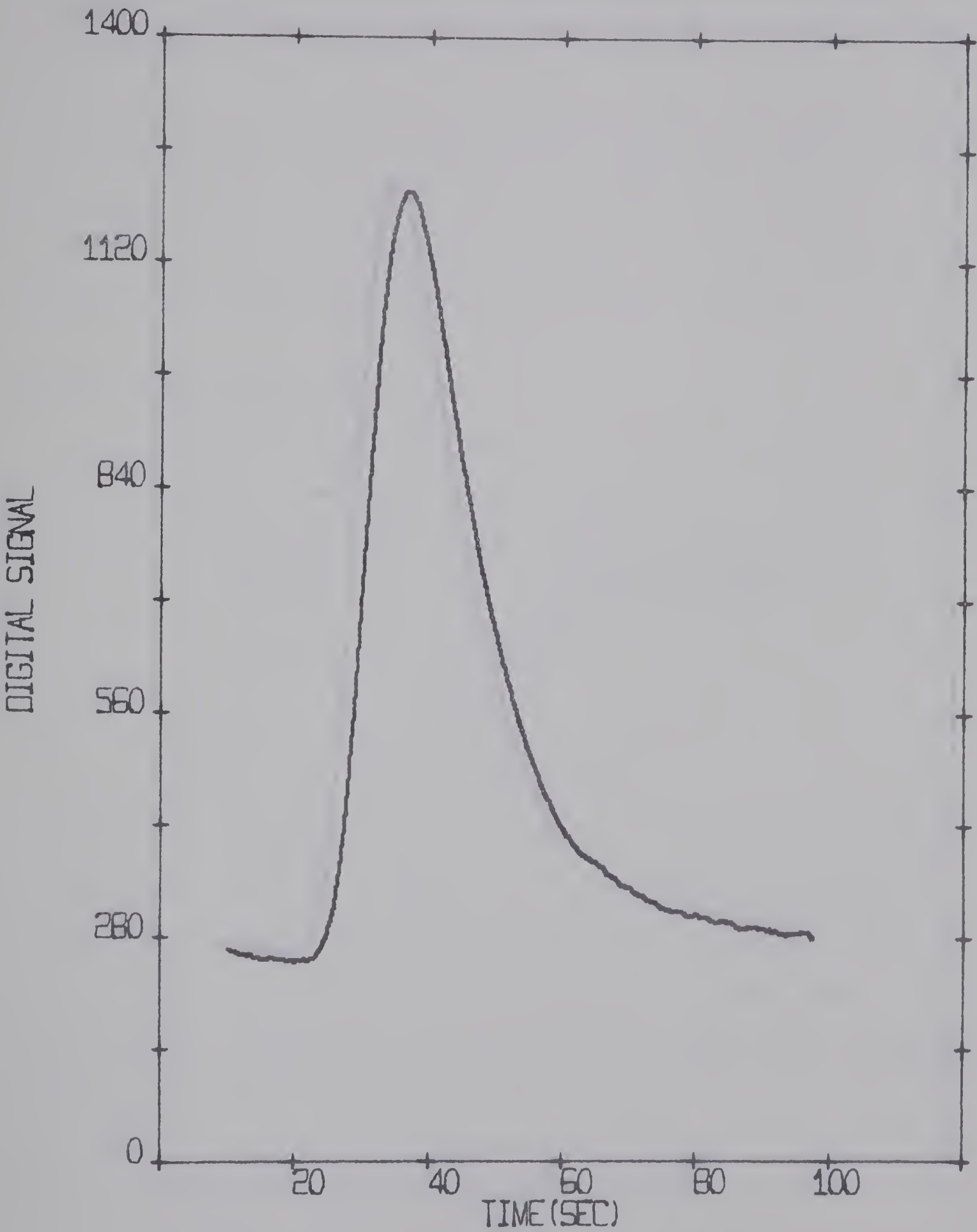


FIGURE 5-17 D
EXPONENTIAL FILTER ON SIGNAL ALPHA=0.1

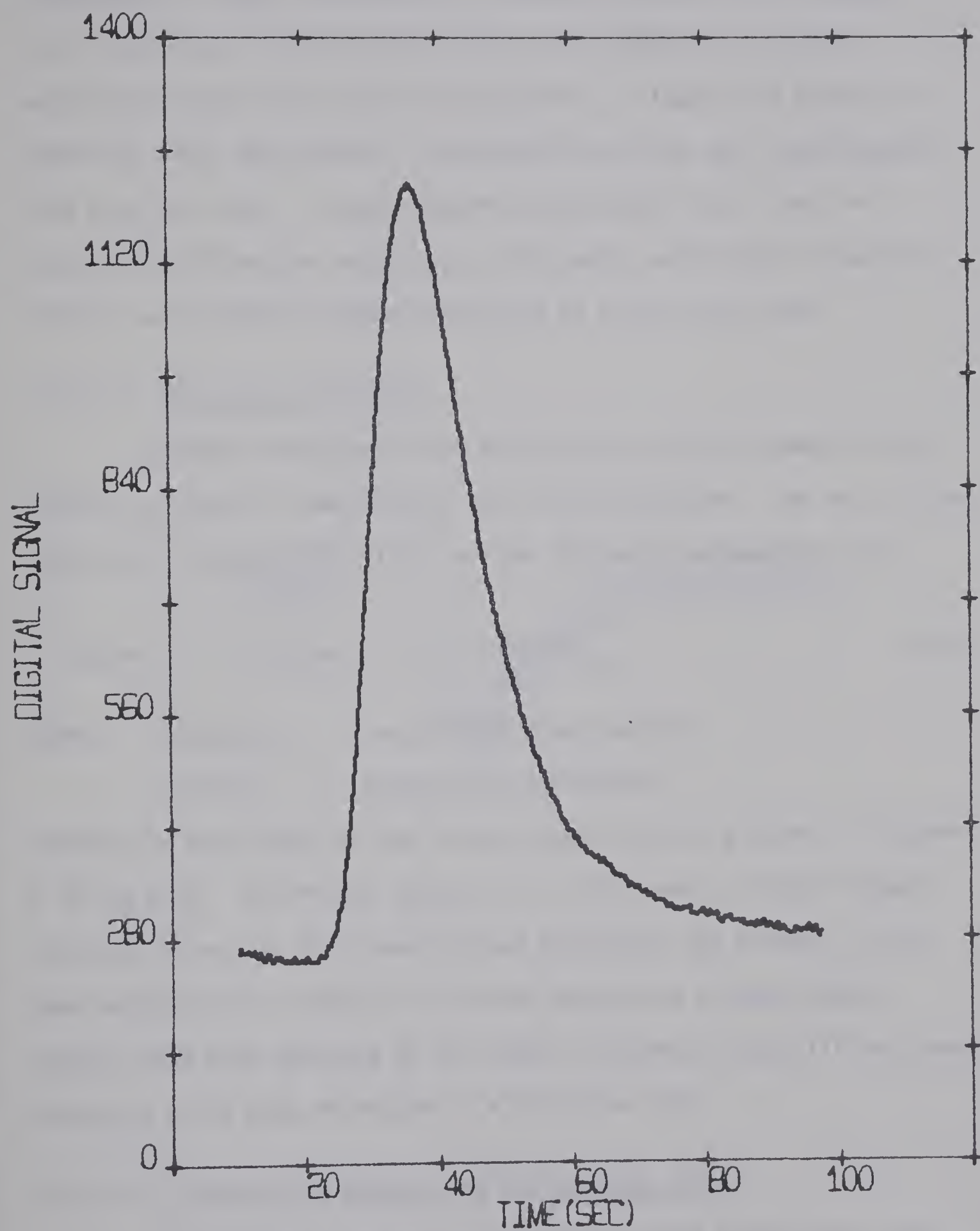


FIGURE 5-17 E

13 POINT 3 RD ORDER AND SPIKE FILTER

represented a large contribution of the past points to the present point, but due to the high scan rate of 16 points per second no appreciable peak distortion or lag occurred. Figure 5.18 shows the resulting first derivative. The second derivative was indistinguishable from the noise. It was therefore concluded that it was not possible to filter the raw signal sufficiently with these filters to obtain a well defined second derivative at a high scan rate.

5.13.1.2 Derivative Filtering

Direct filtering of the derivatives yielded somewhat better results, at least in the case of the first derivative. The only filter tried was an exponential filter of the following mathematical form

$$(dy/dx)'_n = \alpha(dy/dx)'_n + (1 - \alpha)(dy/dx)'_{n-1} \quad (5.4)$$

where: $(dy/dx)'_{n-1}$ = last filtered derivative
 $(dy/dx)'_n$ = present raw derivative

Results for two values of the filter factor (α) are plotted in Figures 5.19 and 5.20. The filter factor of $\alpha = 0.02$ used to obtain Figure 5.20 was low enough that some lag and distortion was evident. This same technique when used on the second derivative yielded better results than were obtained by raw signal filtering, but still not good enough to allow peak detection at a high scan rate.

5.13.1.3 Filtering to Improve the Optimal Scan Rate

The optimal scan rate was defined as the fastest scan rate that resulted in a well defined peak detection. By use of filters the optimal scan rate for a given peak could be raised. Only one filtering scheme was employed to accomplish this. The raw signal was spike

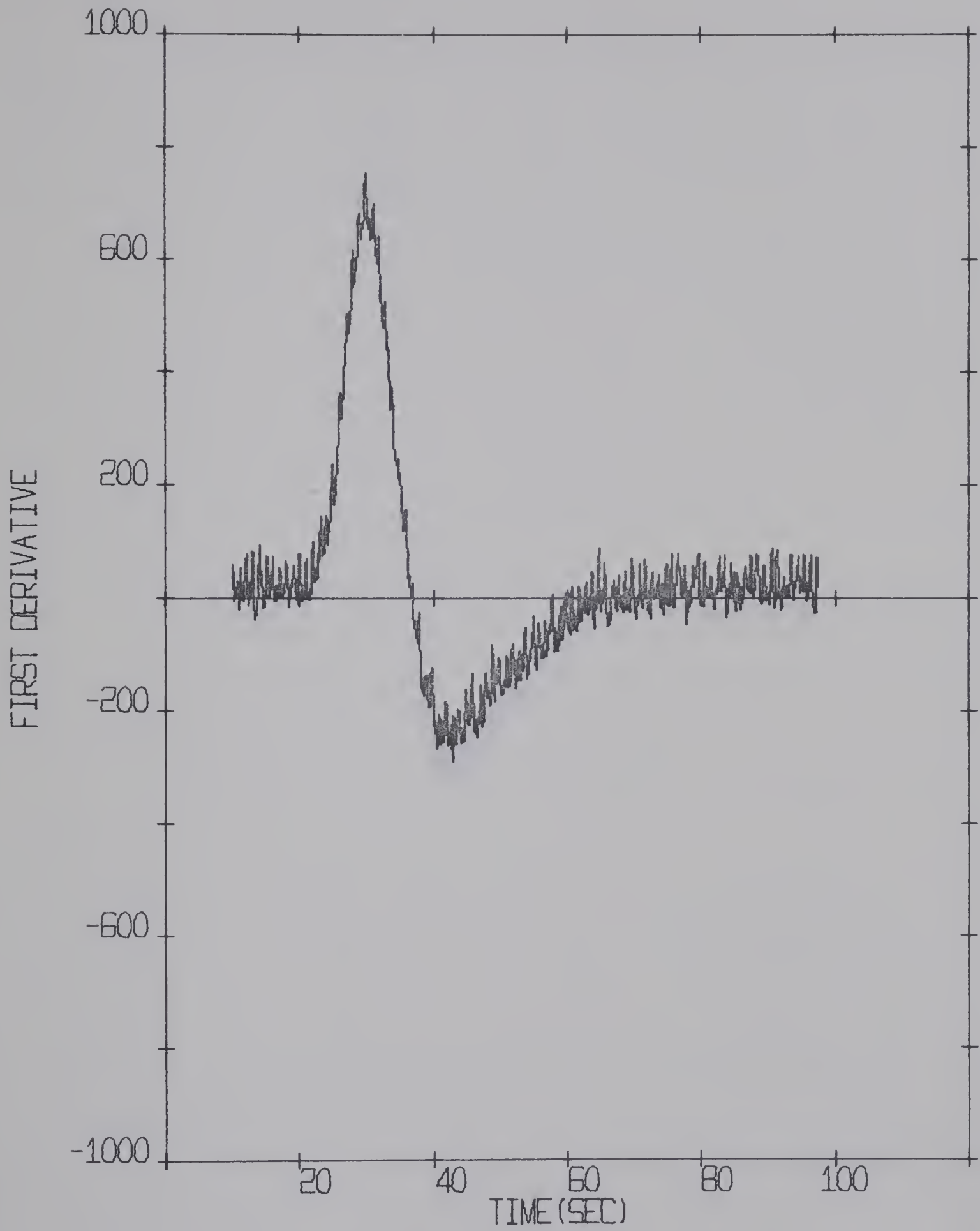


FIGURE 5-18

EXPONENTIAL FILTER ON SIGNAL ALPHA=0.1

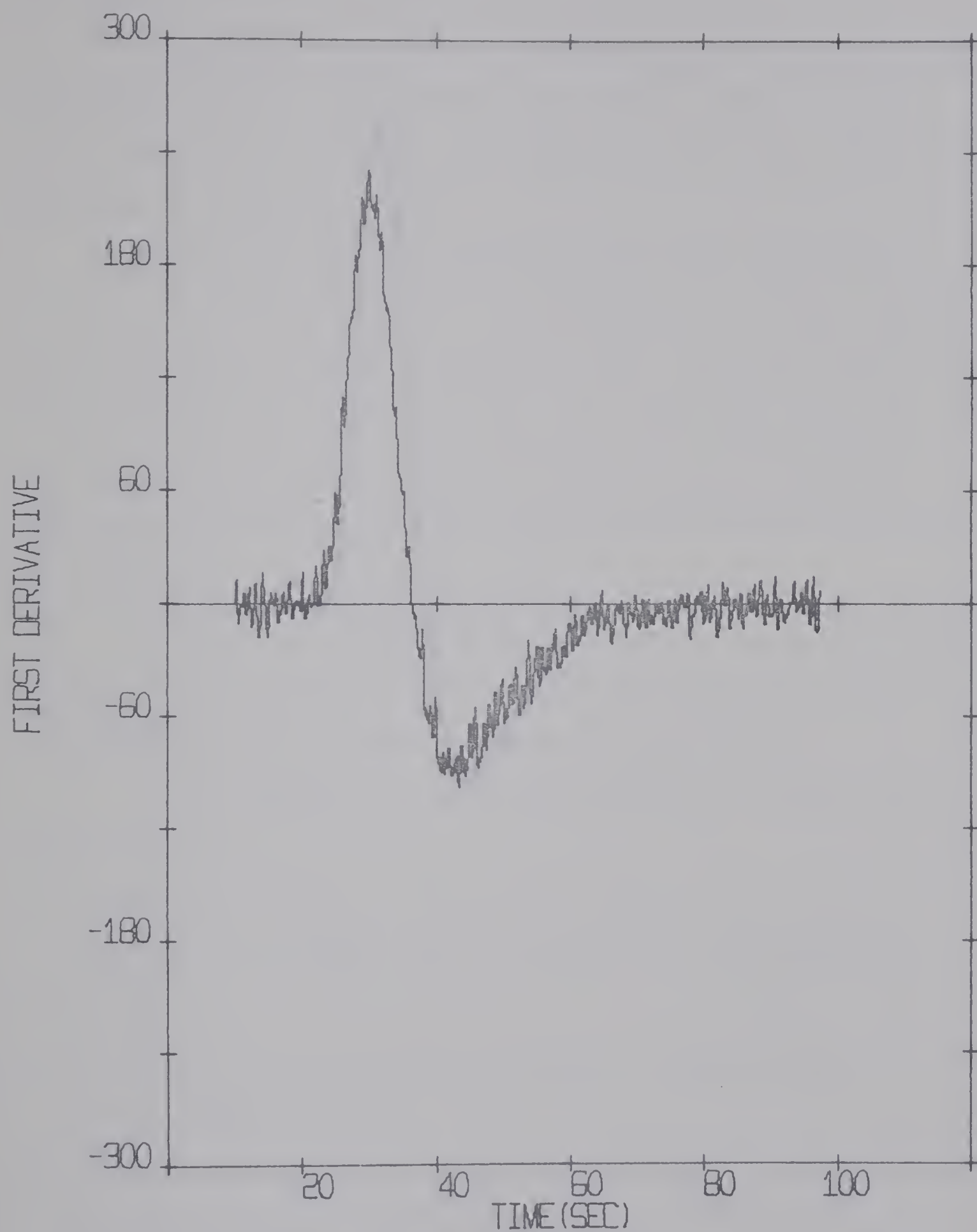


FIGURE 5-19

EXPONENTIAL FILTERING ON FIRST DERIVATIVE $\text{ALPHA}=0.10$

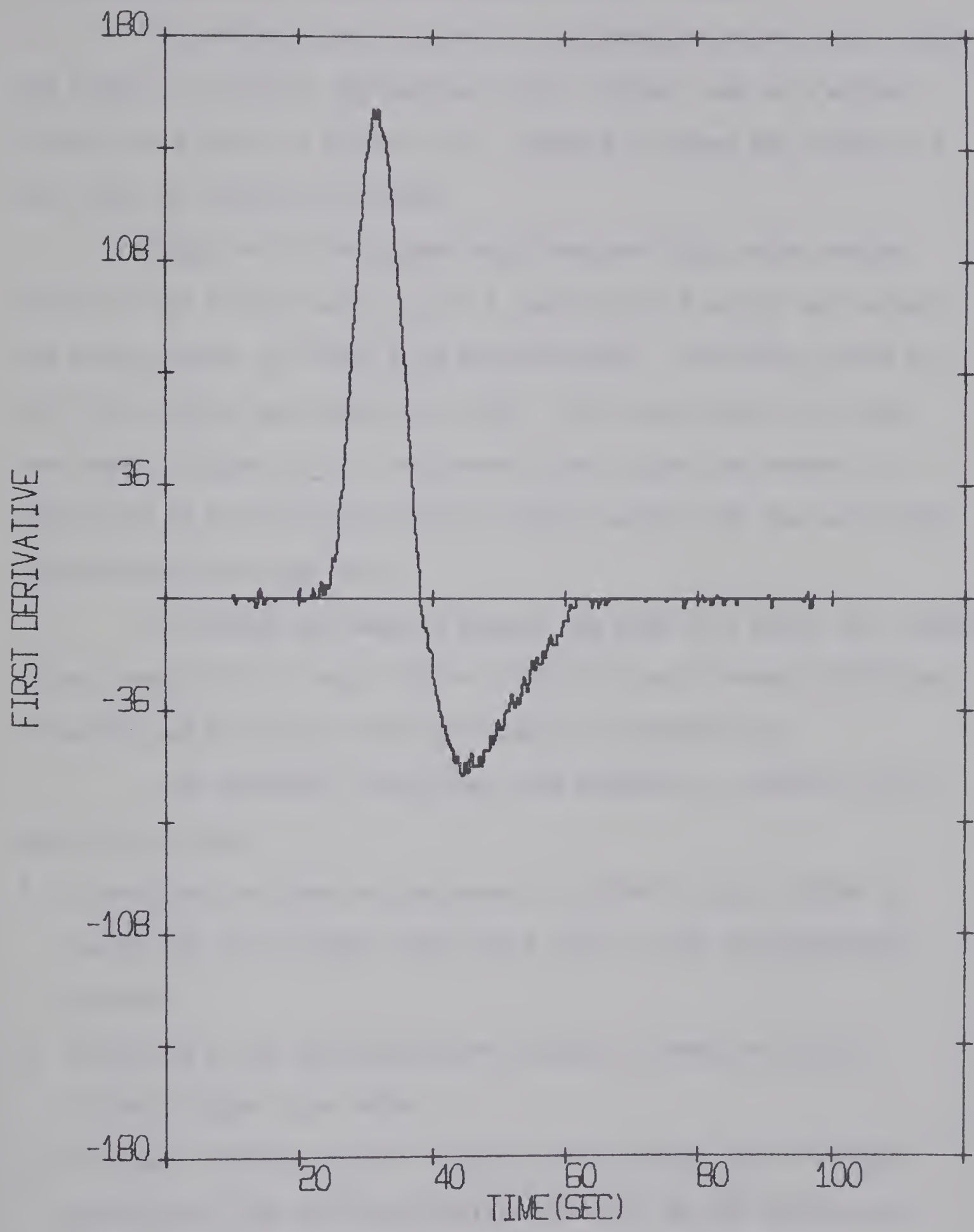


FIGURE 5-20

EXPONENTIAL FILTERING ON FIRST DERIVATIVE ALPHA=0.02

filtered and the derivatives were exponentially filtered.

The optimal scan rate for no filtering was found to be 1 point per second. The first derivative of this optimal scan rate without filters was plotted in Figure 5.21. Figure 5.22 shows the effect of a scan rate of 2 points per second.

Using the filter scheme described previously with various values of the filter factor (α) at a scan rate of 2 points per second the results shown in Figure 5.23 were obtained. The optimal value of the filter factor was found to be 0.06. The results for this value are shown in Figure 5.23c. Any lower values caused too severe of a repression of the derivative and any higher values left too much noise to distinguish the peak end.

An attempt was made to advance the scan to 4 points per second. It was impossible to find a filter factor that would provide sufficient filtering and not distort the peak shape or introduce lag.

Four important conclusions were reached as a result of this part of the study.

1. A variable scan rate was necessary to allow the scan routine to handle the varying peak shapes that occur in gas chromatographic analyses.
2. Filtering of the derivatives and raw data allowed the use of slightly higher scan rates.
3. The peak finishes could be observed more exactly using filtered derivatives than unfiltered derivatives even at the optimum scan rate. This was observed in Figure 5.23c (2 pps, filtered) and Figure 5.21 (1 pps, unfiltered). The second derivative of Figure 5.23c gave a peak end closer to the true value observable in

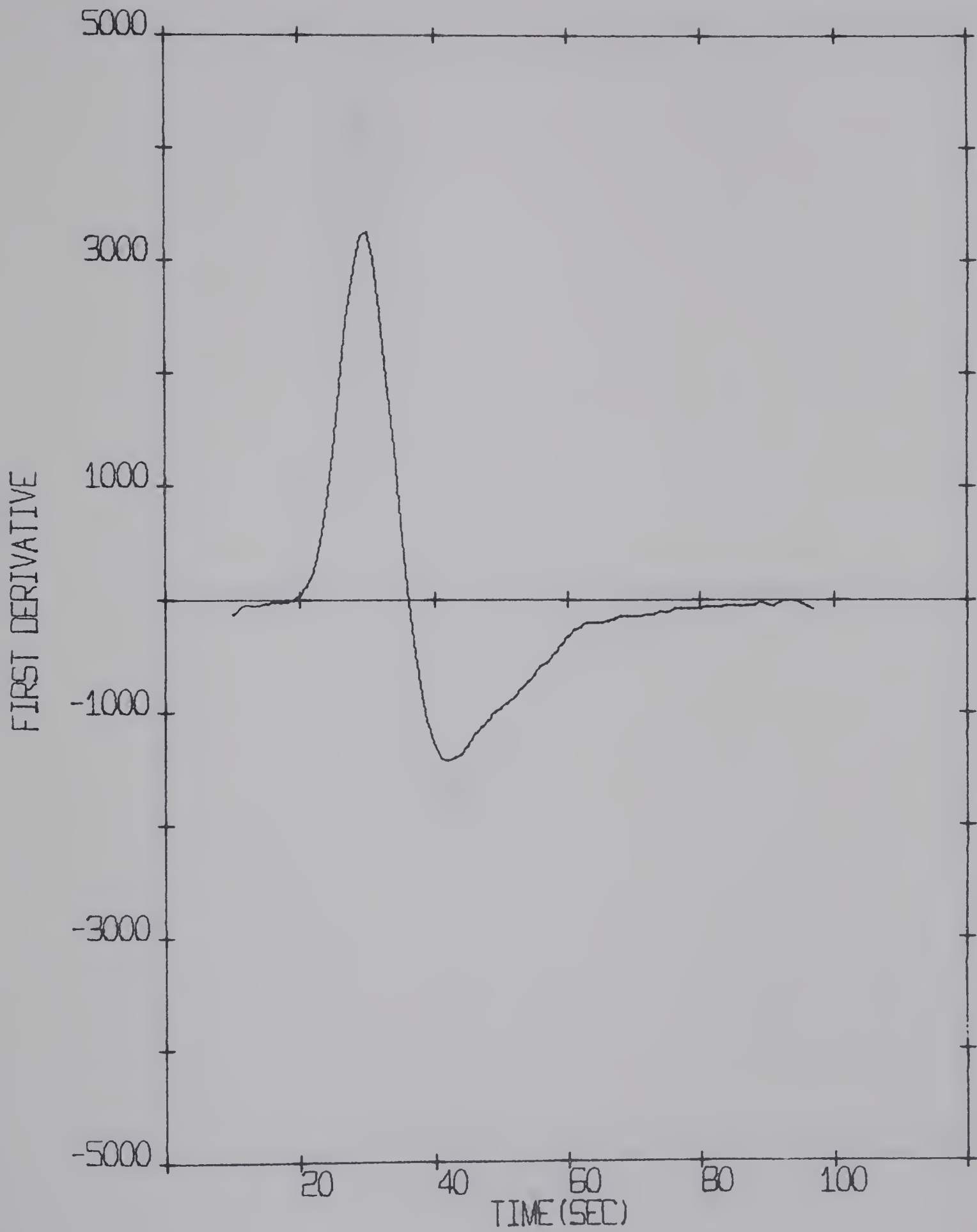


FIGURE 5-21
OPTIMAL SCAN RATE (1 PPS.) NO FILTER

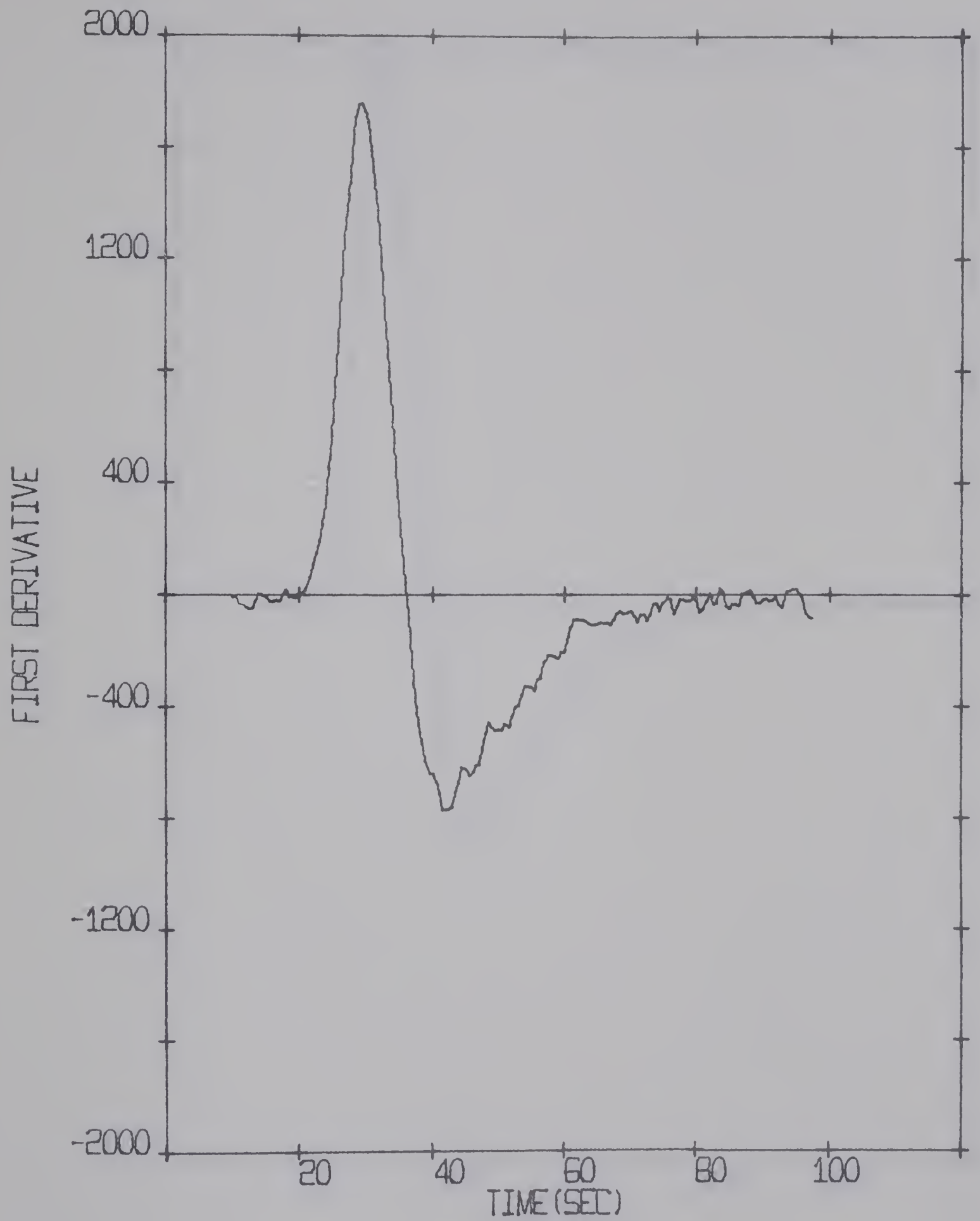


FIGURE 5-22
2 PPS. NO FILTER

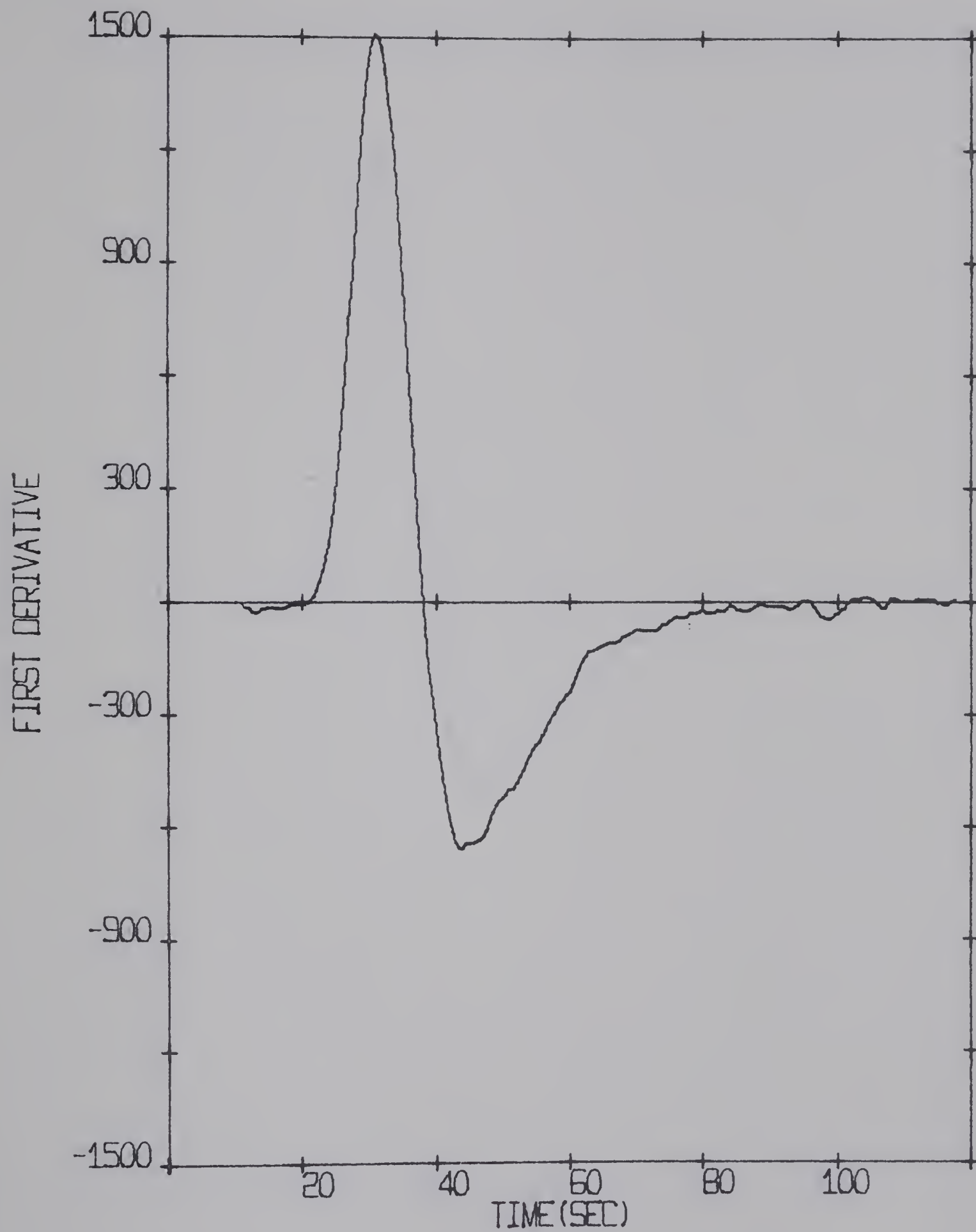


FIGURE 5-23 A

DERIVATIVE FILTERING (2 PPS) ALPHA=0.20

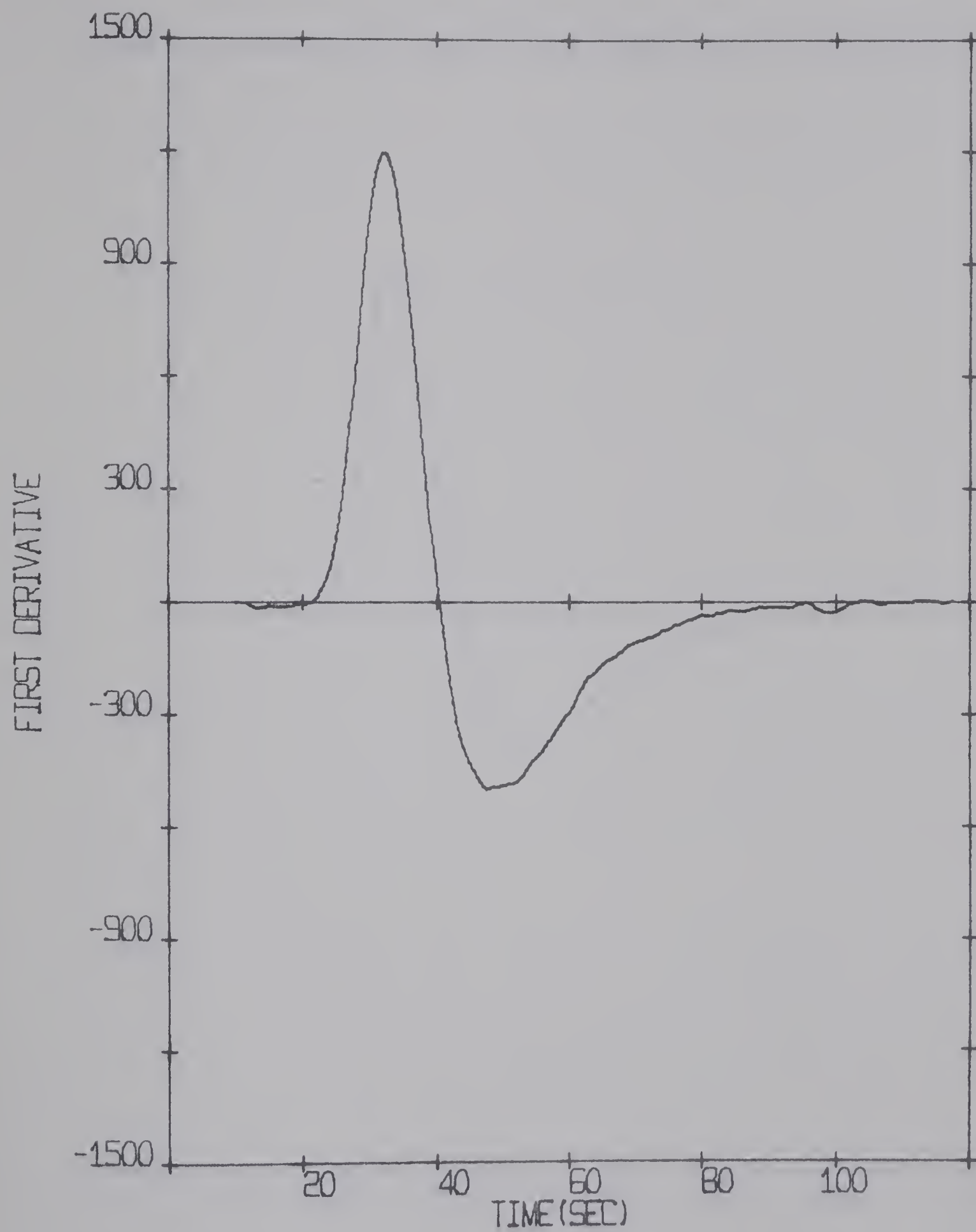


FIGURE 5-23 B

DERIVATIVE FILTERING (2 PPS) ALPHA=0.10

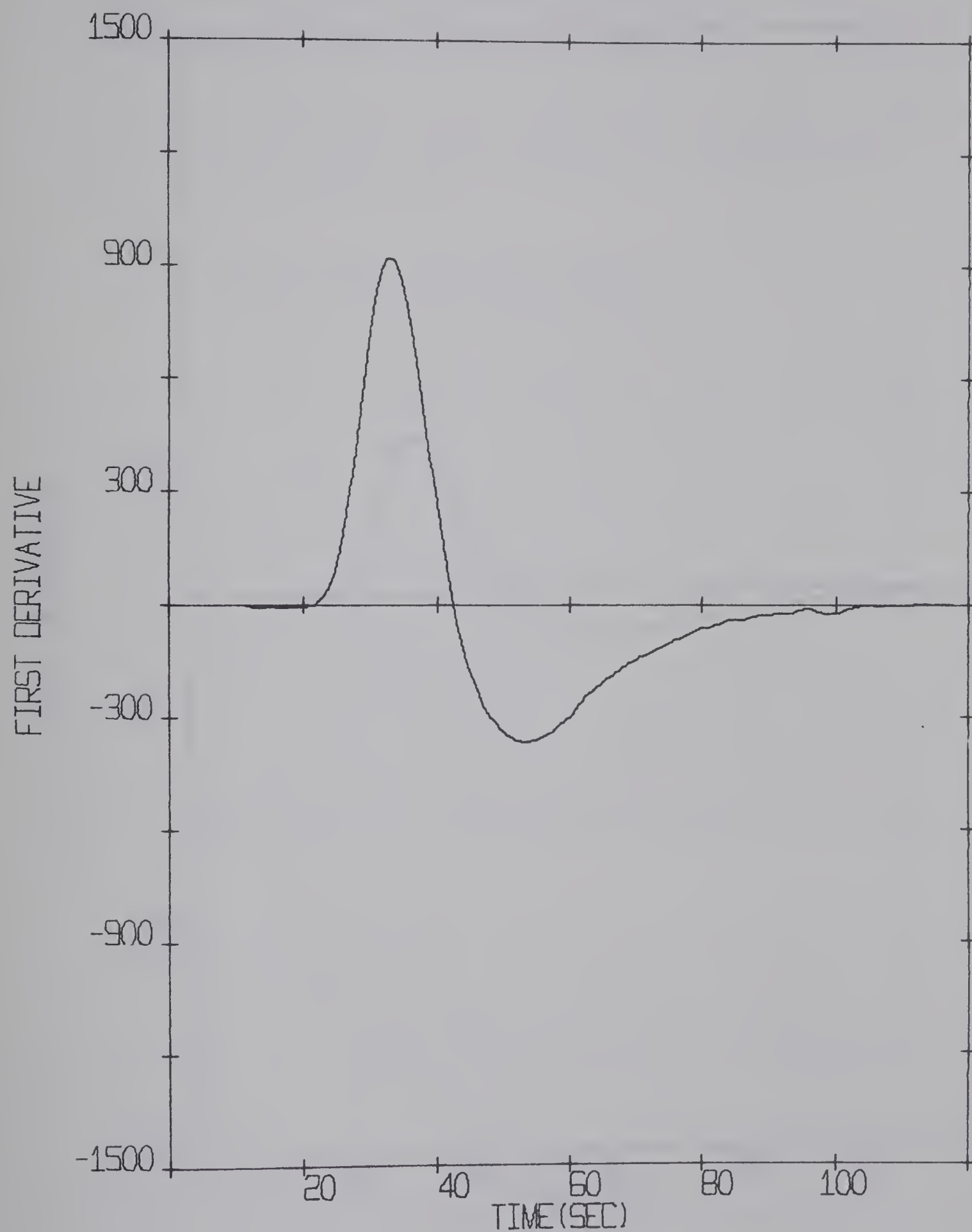


FIGURE 5-23 C

DERIVATIVE FILTERING (2 PPS) $\text{ALPHA}=0.06$

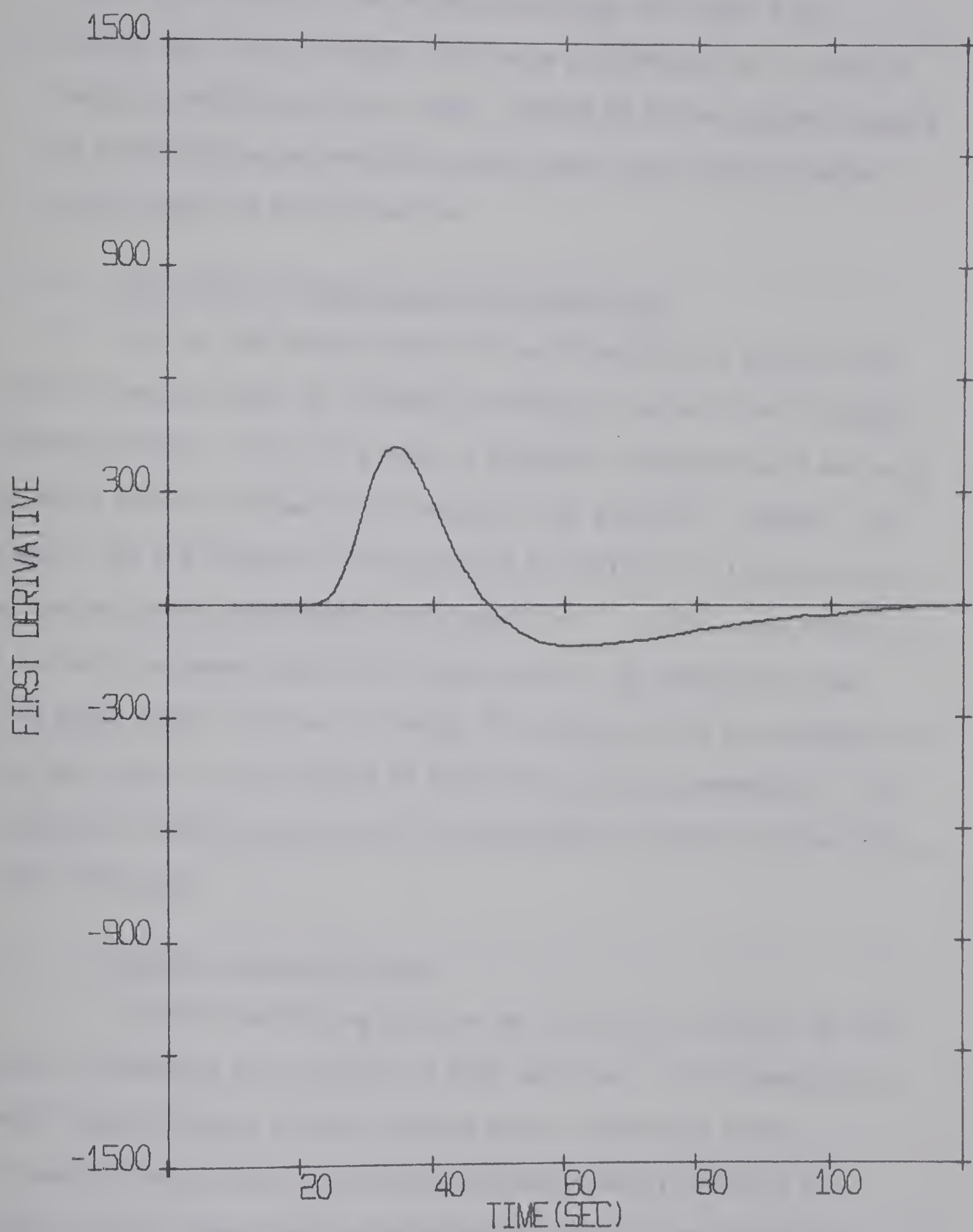


FIGURE 5-23 D

DERIVATIVE FILTERING (2 PPS) ALPHA=0.02

Figure 5.15 than did the second derivative of Figure 5.21.

4. None of the filter schemes tried were as effectual or as easy to apply as reduction of scan rate. Values of filter factors capable of sufficient noise reduction were always very close to values that caused lag and distortion.

5.13.2 Application of Programmable Gain Amplifier

Due to the noise effects it was found that it was not possible to monitor peaks of extremely different size with the required reproducibility. For this project a hardware programmer unit was used to apply varying attenuations throughout the analysis. However, for general use the computer package should be modified to take advantage of the available programmable gain amplifier. The ADC range should be a variable parameter specified by the user at job definition time. This would enable the user to change ADC ranges during the analysis in the same manner as scan rates or the other variable parameters. The integration routine would have to be modified to correct for the ADC range being used.

5.13.3 Parameter Change on Status

For this monitoring program and all others familiar to this author, parameters are varied on a time basis only. This makes parameter changes between closely eluting peaks a difficult matter. Fortunately peaks that resolve close together usually exhibit a similar general shape and can be detected with the same parameters. An exception to this rule occurred with two peaks encountered in this research program, SO_2 , and H_2O . The optimum scan rate for the first peak (SO_2) was 2 points per second, while the optimum scan

rate for the second peak (H_2O) was 1 point per second. The first peak was not detected properly at 1 point per second and the second peak was not detected properly at 2 points per second. The short time separation between the peaks made it difficult to choose the time for scan rate change.

A possible scheme for the implementation of this feature would require a time band, the status, and a default status. The time band would allow the package to only look for the status change for a short period of time, but a long enough time to always include the change. The default status would allow for such things as a start of the second peak without a return to the baseline.

5.13.4 Treatment of Unresolved Peaks

The simple methods included in the package were shown to be inadequate for all but very slightly fused peaks or true shoulders. Furthermore, the information required to apply these methods was almost as rigorous as that required to apply more sophisticated methods with a stronger theoretical basis.

A review of a general method of obtaining information from unresolved peaks has been compiled from some of the many recent publications on the subject. The methods can be divided into the 2 following groups.

1. Iterative fitting of the data to obtain the true peak form.
2. On-line methods requiring only a small amount of information about the peaks.

Most of the methods of resolving peaks appearing in the literature were off-line iterative procedures (1,2,13,14,19,20,21,23,27). The main difference in these methods was the functional form assumed for the peak

shape. All of the methods required a standard run on the separate component peaks to obtain their various shape factors.

A method applicable to an on-line system has been discussed by Hancock et al (23,24). The peaks were assumed to be represented by bi-Gaussian functions with the following form:

$$y = A \exp - [(t - b)/c]^2 \quad (5.5)$$

$$\begin{array}{ll} \text{if } t \leq b & c = c_1 \\ t > b & c = c_2 \end{array}$$

where:

A = amplitude

c_1, c_2 = shape factors

b = retention time

The parameters c_1 and c_2 were determined by a separate run on each of the components. If two peaks are fused there will be two maximums at (y_1, t_1) and (y_2, t_2) . These maximums are the sums of the individual peaks at t_1 and t_2 .

$$y_1 = A_1 \exp - [(t_1 - b_1)/c_1]^2 + A_2 \exp - [(t_1 - b_2)/c_2]^2 \quad (5.6)$$

$$y_2 = A_1 \exp - [(t_2 - b_1)/c_1]^2 + A_2 \exp - [(t_2 - b_2)/c_2]^2 \quad (5.7)$$

With no assumptions the four unknowns b_1 , b_2 , A_1 , and A_2 are soluble by employing the fact that the first derivatives at the maximums were zero. However, the problem is simplified to allow for on-line calculation by assuming that $t_1 = b_1$ and $t_2 = b_2$. This yields the following two equations:

$$y_1 = A_1 + A_2 \exp - [(t_1 - t_2)/c1_2]^2 \quad (5.8)$$

$$y_2 = A_1 \exp - [(t_2 - t_1)/c2_1]^2 + A_2 \quad (5.9)$$

The total area measured for the fused peaks is then divided as follows:

$$AR_1 = \frac{A_1 (c1_1 + c2_1)}{A_1 (c1_1 + c2_1) + A_2 (c1_2 + c2_2)} \times AR_T \quad (5.10)$$

where

AR_1 = area of peak 1

AR_T = total area of fused peaks

Hancock et al evaluated this method in comparison with the empirical methods of dropping perpendiculars and using tangents for shoulders. This mathematical method was always superior to the two empirical methods. The mathematical method yielded areas for the smaller peak within three to four per cent of the true area. Anderson (1,2) has reported accuracies of ± 0.5 per cent for an iterative technique. Some improvement to the method of Hancock et al (23,24) could result from substituting other functional forms in specific analyses. The specific analysis would first have to be treated to find the best functional form and the appropriate parameters.

5.14 Reproducibility of Analyses

Reproducibility of the integration device was the main consideration in obtaining an accurate calibration equation. In order to compare the reproducibility of the computer to a mechanical disc integrator, a sample of SO_2 in N_2 was prepared in the calibration cylinder described in Appendix B. This well mixed sample was analysed six times with simultaneous monitoring by both devices. The

reproducibilities of the integrations were then checked by calculating the average absolute deviations for the area ratios of SO_2 to N_2 . Finally in order to ascertain the precision of the analysis, the area ratios were converted to mole percentages and the value of the error was expressed in mole per cent units. The results are tabulated in Table 5.5. The computer has a reproducibility of ± 0.003 mole per cent while the disk integrator has a reproducibility of ± 0.012 mole per cent.

In order to demonstrate the ability of the computer to extend the range of the acceptable accuracy, a trace sample of H_2S in N_2 was prepared. The sample was analysed six times. The disk integrator was not sensitive enough to integrate this very small peak. The computer detected the peak every time with still acceptable reproducibility. The results are shown in Table 5.6.

TABLE 5.5
INTEGRATION REPRODUCIBILITY ON SO_2 PEAK

	Mechanical Integrator	Computer
area ratio	0.018506	0.018695
average absolute deviation of		
area ratio	± 0.000170	± 0.000041
mole per cent SO_2	1.41797	1.43173
average absolute deviation as mole		
per cent	± 0.012	± 0.003
average per cent error	± 0.85	± 0.21

TABLE 5.6
INTEGRATION SENSITIVITY ON H₂S PEAK*

	Computer
area ratio	0.000408
average absolute deviation of area ratio	± 0.000048
mole percent H ₂ S	0.12592
average absolute deviation as mole percent	± 0.0041
average percent error	± 3.25

* not detected by the disk integrator

5.15 Summary and Recommendations

Use of computer monitoring of the gas chromatograph leads to increased reproducibility and high sensitivity. The immediate results available to the operator enabled the use of on-line data reduction which resulted in a substantial saving of time and enabled the operator to chose the steady states at which data were taken.

The analysis of the computer package exemplified the importance of a variable scan rate. Tests with the various filters demonstrated that the best of these filters can only be used to increase the scan rate slightly or to improve the peak characteristics at the optimum scan rate.

It is recommended that the following modifications be made to improve the package further.

1. Remove the present inadequate filters and replace them with exponential filters on the derivatives.
2. The programmable gain amplifier should be implemented to take full

advantage of the possible added resolution.

3. The option of "parameter changes on status" should be implemented.
4. The method of Hancock et al should be tested to ascertain its capabilities with fused peaks. If the scheme appears useful it should be implemented.

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APPENDIX A

CALIBRATION OF PROCESS MEASUREMENTS

A.1 Differential Pressure Transducer

Due to the improved feed pressure control discussed in section 3 of Chapter 3 it was necessary to only calibrate the feed flow at one feed pressure. It was found that a feed pressure of 22.5 psia was adequate for the range of flow rates used in this study.

The electronic feed differential pressure transducer was calibrated against a pre-calibrated dry test meter using pure nitrogen. A calibration equation of the following form was then fit to the data.

$$F_{N_2} = a_0 + a_1 \times \sqrt{PCT} + a_2 \times PCT \quad (A.1)$$

where

F_{N_2} = volumetric feed rate (SCFH)

PCT = transducer output (per cent)

a_0, a_1, a_2 = least squares fit parameters.

This equation was found to the measured flow rate accurately in the range of 2 to 100 per cent of the transducer output. Below 2 per cent the fit errors generally became greater than 1 per cent with respect to the volumetric feed flow. The results of a calibration are contained in Tables A.1, A.2 and A.3.

A.2 Reactor Pressure Transducer

The reactor pressure transducer was calibrated at a temperature of 500°K. McGregor (34) had found that shifts in calibration due to temperature changes were insignificant at elevated temperatures.

TABLE A.1

EXPERIMENTAL RESULTS FOR D/P CELL CALIBRATION

TIME FOR 1 CUBIC FOOT OF GAS FLOW (MINUTES)	ATMOSPHERIC PRESS (MM HG)	TEMP (DEG F)	FOXBORO RECORDER D/P CELL (PCT)	IBM 1800 ABS PRESS COMPUTER (PCT)	IBM 1800 COMPUTER (PCT)
36.000	708.0	77.7	3.00	30.00	3.36
22.667	708.0	78.0	7.30	30.00	7.62
14.042	708.0	78.2	18.20	30.00	18.27
10.633	708.0	78.8	32.30	30.00	32.21
8.973	708.0	79.5	45.10	30.00	44.90
8.143	708.0	79.6	54.40	30.00	54.02
7.080	708.0	80.0	71.30	30.00	70.93
6.070	708.0	80.0	96.40	30.00	95.82

TABLE A.2

CALCULATED RESULTS FOR D/P CELL CALIBRATION

RUN NO.	FEED FLOW METERING SYSTEM			FLOW RATE (SCFH)
	ABS PRESS (PSIA)	D/P CELL SQRT(PCT)	COMPUTER SQRT(PCT)	
1	20.62	1.31	1.35	1.50
2	20.62	1.64	1.66	2.38
3	20.62	2.06	2.06	3.84
4	20.62	2.38	2.38	5.07
5	20.62	2.59	2.58	6.00
6	20.62	2.71	2.71	6.61
7	20.62	2.90	2.90	7.60
8	20.62	3.13	3.12	8.86

TABLE A.3

D.P. CELL CALIBRATION EQUATION

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$$X = \text{SQRT}(PCT)$$

$$Y = SCFH$$

THE COEFFICIENTS OF THE POLYNOMIAL ARE

$$A0 = -0.04202$$

$$A1 = 0.89619$$

$$A2 = 0.00104$$

REGENERATED DATA

X MEASURED	Y OBSERVED	Y CALCULATED	PCT ERROR
1.732	1.501	1.513	0.789
2.701	2.383	2.387	0.151
4.266	3.845	3.800	1.185
5.683	5.073	5.085	0.233
6.715	6.004	6.023	0.327
7.375	6.614	6.624	0.153
8.443	7.602	7.600	0.030
9.818	8.867	8.858	0.104

$$\text{VARIANCE} = 0.000421$$

$$\text{STANDARD DEVIATION} = 0.020540$$

$$\text{MAXIMUM PCT ERROR} = 1.185642$$

TABLE A.4

REACTOR ABSOLUTE PRESSURE TRANSDUCER CALIBRATION

X=FOXBORO CHART RECORDER PERCENT
Y=MM. HG.

THE COEFFICIENTS OF THE POLYNOMIAL ARE

$$A_0 = 716.47387$$

$$A_1 = 6.54523$$

REGENERATED DATA

X MEASURED	Y OBSERVED	Y CALCULATED	PCT ERROR
5.500	751.800	752.472	0.089
8.300	771.600	770.799	0.103
21.500	857.100	857.196	0.011
27.800	898.400	898.431	0.003

$$\text{VARIANCE} = 0.368025$$

$$\text{STANDARD DEVIATION} = 0.606651$$

$$\text{MAXIMUM PCT ERROR} = 0.103797$$

The transducer was calibrated against a mercury manometer by closing the reactor product outlet line and varying the setpoint on the feed pressure controller. The reactor pressure was then correlated to the transducer output by a least squares fit of the following form:

$$P = a_1 \times \text{PCT} + a_0 \quad (\text{A.2})$$

where P = reactor pressure (mm Hg)

PCT = transducer output (per cent)

a_0, a_1 = fit parameters

A typical set of calibration data and the resulting least squares fit follow in Table A.4.

A.3 Water Feeder

The syringe pump was calibrated over the range of interest by a gravimetric procedure. A small glass weighing bottle with a capillary tube stopper was used to collect the sample. The syringe outlet just fit the capillary stopper to reduce evaporation effects. The weight of the water collected over a timed interval was converted to the volume of water taking into account the effect of temperature on density^{*}. A calibration equation of the following form was then fit to the data.

$$V_{\text{H}_2\text{O}} = a_1 \times \text{PCT} + a_0 \quad (\text{A.3})$$

where $V_{\text{H}_2\text{O}}$ = volumetric feed rate (ml/hr)

PCT = pump setting (per cent)

a_1, a_0 = fit parameters

Table A.5 is a least squares fit of the temperature-density correlation for water. Table A.6 is the fit of the calibration data.

^{*}Perry, J.H., Chemical Engineers Handbook (New York: McGraw-Hill Book Company, 1963) p. 3-70.

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TABLE A.5

DENSITY OF WATER AS A FUNCTION OF TEMPERATURE

X=TEMPERATURE (DEG. F)
Y=DENSITY OF WATER (GM/CC)

THE COEFFICIENTS OF THE POLYNOMIAL ARE

$$A_0 = 1.00597$$

$$A_1 = -0.00011$$

REGENERATED DATA

X MEASURED	Y OBSERVED	Y CALCULATED	PCT ERROR
60.000	0.999	0.999	0.008
64.000	0.998	0.998	0.002
68.000	0.998	0.998	0.002
72.000	0.997	0.997	0.000
76.000	0.997	0.997	0.019
80.000	0.996	0.996	0.016

$$\text{VARIANCE} = 0.000000$$

$$\text{STANDARD DEVIATION} = 0.000120$$

$$\text{MAXIMUM PCT ERROR} = 0.019002$$

TABLE A.6

CALIBRATION OF WATER FEED PUMP SEPT 23/71

X=PERCENT READING (1/100 SCALE)
Y=CC H2O/HR

THE COEFFICIENTS OF THE POLYNOMIAL ARE

A0 = 0.15581

A1 = 0.52044

REGENERATED DATA

X MEASURED	Y OBSERVED	Y CALCULATED	PCT ERROR
10.000	5.468	5.360	1.976
17.500	9.213	9.263	0.544
25.000	13.026	13.166	1.081
40.000	21.056	20.973	0.394

VARIANCE = 0.013650

STANDARD DEVIATION = 0.116834

MAXIMUM PCT ERROR = 1.976511

MAINLINE FDCAL

MAINLINE FDCAL

```

C *****
C *
C *          MAINLINE FDCAL
C *
C * THIS PROGRAM WAS WRITTEN TO DOCUMENT THE
C * CALIBRATION DATA TAKEN ON THE FEED D/P CELL, REDUCE
C * THE DATA TO USEFUL UNITS OF FLOW AND MEASUREMENT
C * AND PUNCH THE CALCULATED RESULTS OUT ON CARDS TO
C * PROVIDE INPUT FOR A LEAST SQUARES FITTING PROGRAM
C * INPUT DATA
C *   N          - NUMBER OF CALIBRATION RUNS
C *   NPAGE      - PAGE NUMBER OF FIRST PAGE OF OUTPUT
C *   NCOPY      - NUMBER OF COPIES OF OUTPUT DESIRED
C *   NR         - RUN NUMBER
C *   A(I,1)     - TIME REQUIRED FOR ONE CU FT OF GAS
C *               FLOW (MIN)
C *   A(I,2)     - ATMOSPHERIC PRESSURE (MM HG)
C *   A(I,3)     - ROOM TEMPERATURE (DEG F)
C *   A(I,4)     - RECORDER READING (D/P CELL)
C *   A(I,5)     - RECORDER READING (ABS PRESS)
C *   A(I,6)     - COMPUTER READING (D/P CELL)
C *   A(I,7)     - DRY TEST METER CALIBRATION FACTOR
C *
C *****

```

```

      DIMENSION A(40,7),NR(40),FLO(40)
      READ(5,9) N,NPAGE,NCOPY
9  FORMAT(3I5)
      DO 2 I=1,N
      READ(5,1) NR(I),(A(I,J),J=1,7)
2  CONTINUE
1  FORMAT(I5,5X,7F10.5)
      DO 5 NC=1,NCOPY
      WRITE(6,3) NPAGE
3  FORMAT('1', ///66X,'A-',I2,//////
1      35X,'TABLE A.13'/// ,18X
      *,'EXPERIMENTAL RESULT
      1S FOR D/P CELL CALIBRATION'/ )
      WRITE(6,4)
4  FORMAT( 10X,'TIME FOR 1      ATMOSPHERIC      FOXBORO
      * RECORDER      IB
      2M 1800'/ 10X,'CUBIC FOOT    PRESS      TEMP    D/P CELL
      * ABS PRESS CO
      3MPUTER' / 10X,'OF GAS FLOW  (MM HG) (DEG F)    (PCT)
      *      (PCT)
      4(PCT) '/ 11X,'(MINUTES)'/)
      DO 5 I=1,N
5  WRITE(6,6) (A(I,J),J=1,6)

```


MAINLINE FDCAL

...(CONT'D)

```

6  FORMAT(13X,F6.3,5X,F5.1,5X,F4.1,4X,F5.2,6X,F5.2,5X
   *,F5.2)
   NPAGE=NPAGE+1
   DO 7 NC=1,NCOPY
   WRITE(6,20)NPAGE
20  FORMAT('1', ////,66X,'A-',I2,////)
   WRITE(6,10)
10  FORMAT( ///,32X,'TABLE A.14'// 15X,'CALCULATED RESULTS
   * FOR D/P CEL
   1L CALIBRATION'//)
   WRITE(6,11)
11  FORMAT(16X,'RUN          FEED FLOW METERING SYSTEM      FLOW'
   */ 16X,'NO.
   1ABS PRESS  D/P CELL    COMPUTER  RATE'/ 22X,'(PSIA)
   * Sqrt(PCT) SQ
   2RT(PCT) (SCFH)'//)
   DO 7 I=1,N
   TPCOR=A(I,2)/760.*520./(A(I,3)+460.)
   FLO(I)=TPCOR*1./A(I,1)*60.*A(I,7)
   A(I,4)=A(I,4)**0.5
   A(I,6)=A(I,6)**0.5
   A(I,5)=A(I,5)*0.25+15.
   WRITE(6,8) NR(I),A(I,5),A(I,4),A(I,6),FLO (I)
7  CONTINUE
8  FORMAT(14X,I5,3X,F5.2,1X,3(5X,F5.2))
   READ(5,44) I
44  FORMAT(I1)
   GO TO (14,40),I
14  CONTINUE
   WRITE(5,102)
102 FORMAT('FDCAL OUTPUT FOR LST. SQ. ')
   DO 12 I=1,N
   12 WRITE(5,100) A(I,4),FLO(I),NR(I),A(I,5)
   DO 13 I=1,N
   13 WRITE(5,100) A(I,6),FLO(I),NR(I),A(I,5)
100 FORMAT(2F10.5,40X,I3,2X,F5.2)
40  CONTINUE
   CALL EXIT
   END

```


MAINLINE LEAST

MAINLINE LEAST

```

C      ****
C      *
C      *          MAINLINE LEAST
C      *
C      * THIS PROGRAM WAS WRITTEN FOR FITTING A MAXIMUM OF
C      * 50 DATA POINTS TO POWER SERIES TYPE POLYNOMIALS OF
C      * ANY ORDER UP TO A MAXIMUM OF FOURTH DEGREE.
C      * INPUT DATA
C      * NCASE - NUMBER OF SETS OF DATA
C      * NCOPY - NUMBER OF COPIES OF OUTPUT DESIRED
C      * N - NUMBER OF DATA POINTS
C      * M - DEGREE OF POLYNOMIAL
C      * NTL - NUMBER OF CARDS FOR TITLE
C      * NPAGE - PAGE NUMBER OF OUTPUT
C      * NPLT - DATA REGENERATION FLAG
C      *          ...0-REGENERATE GIVEN DATA ONLY
C      *          ...1-REGENERATE GIVEN DATA PLUS 20
C      *          INTERMEDIATE POINTS
C      * DES(K) - ALPHANUMERIC DESCRIPTION OF THE TITLE
C      * XNAME - ALPHANUMERIC DESCRIPTION OF X
C      * YNAME - ALPHANUMERIC DESCRIPTION OF Y
C      * X(I) - INDEPENDENT VARIABLE
C      * Y(I) - DEPENDENT VARIABLE
C      *
C      ****

      DIMENSION X(50),Y(50),A(50,5),P(20,20),V(20),Z(20),
1      IDES(10,15),SNAM(5),XNAME(100),YNAME(100)
      DATA SNAM/'A0 =','A1 =','A2 =','A3 =','A4 ='/
      READ(5,1) NCASE,NCOPY
      DO 9 NC=1,NCASE
      READ(5,1) N,M,NTL,NPAGE,NPLT,IDEC
      IDEC=IDEC+1
1      FORMAT(6I5)
      DO 11 NT=1,NTL
11      READ(5,12) (DES(NT,K),K=1,15)
12      FORMAT(15A4)
      READ (5,20) (XNAME(I),I=1,15)
20      FORMAT (15A4)
      READ (5,21) (YNAME(J),J=1,15)
21      FORMAT (15A4)
13      FORMAT(10X,15A4/)
      MM=M+1
      DO 2 I=1,N
2      READ(5,3) X(I), Y(I)
3      FORMAT(2F10.5)
      DO 4 I=1,N
      DO 4 J=1,MM

```


MAINLINE LEAST

...(CONT'D)

```

4  A(I,J)=X(I)**(J-1)
   DO 5 I=1,MM
   DO 5 J=1,MM
   P(I,J)=0.
   DO 5 K=1,N
5  P(I,J)=P(I,J)+A(K,I)*A(K,J)
   DO 6 I=1,MM
   V(I)=0.
   DO 6 J=1,N
6  V(I)=V(I)+Y(J)*A(J,I)
   GO TO(18,19),IDEC
18 CALL GAUSS(P,V,MM,Z)
   GO TO 22
19 CALL ORIGN(P,V,MM,Z)
22 DO 16 ICOP=1,NCOPY
   WRITE(6,10)
10 FORMAT('1',////)
   DO 17 I=1,NTL
17 WRITE(6,13)(DES(I,K),K=1,15)
   WRITE(6,30)(XNAME(I),I=1,15)
30 FORMAT(///,12X,15A4)
   WRITE(6,31)(YNAME(J),J=1,15)
31 FORMAT(12X,15A4)
   WRITE(6,8)
8  FORMAT(///,10X,'THE COEFFICIENTS OF THE POLYNOMIAL '
1, 'ARE'/)
   DO 15 I=1,MM
15 WRITE(6,7) SNAM(I),Z(I)
7  FORMAT(15X,A4,F11.5/)
16 CALL REGEN(X,Y,Z,MM,N)
   IF(NPLT) 9,9,14
14 CALL POLYT(X,Z,N,MM)
9  CONTINUE
   WRITE(6,99)
99 FORMAT('1')
   CALL EXIT
   END

```


SUBROUTINE ORIGON

SUBROUTINE ORIGON

```

C      ****
C      *
C      *          SUBROUTINE ORIGON
C      *
C      * THE FUNCTION OF THIS SUBROUTINE IS TO SOLVE THE
C      * SET OF EQUATIONS A*X=B USING GAUSSIAN ELIMINATION
C      * AND BACK SUBSTITUTION ROTATING ABOUT THE ELEMENT
C      * OF MAXIMUM MODULUS.
C      *
C      ****

```

```

      SUBROUTINE ORIGN(A,R,N,X)
      DIMENSION A(20,20),R(20),X(20)
      X(1)=0.
      IF(N-2)1,1,2
1      WRITE(6,100)
100  FORMAT(10X,'LST SQ THRU ORIGON INVALID FOR ORDER=1')
      GO TO 500
      2 M=N-1
      DO 11 J=2,M
      S=0.
      DO 12 I=J,N
      U= ABS(A(I,J))
      IF(U-S) 12,12,112
112  S=U
      L=I
      12 CONTINUE
      IF(L-J) 119,19,119
119  DO 14 I=J,N
      S=A(L,I)
      A(L,I)=A(J,I)
      14 A(J,I)=S
      S=R(L)
      R(L)=R(J)
      R(J)=S
      19 IF( ABS(A(J,J))-1.E-30) 115,115,15
115  WRITE(6,3)
      GO TO 500
      15 MM=J+1
      DO 11 I=MM,N
      IF( ABS(A(I,J))-1.E-30) 11,111,111
111  S=A(J,J)/A(I,J)
      A(I,J)=0.0
      DO 16 K=MM,N
      16 A(I,K)=A(J,K)-S*A(I,K)
      R(I)=R(J)-S*R(I)
      11 CONTINUE
      DO 17 K=1,M

```


SUBROUTINE ORIGON

... (CONT'D)

```
I=N+1-K
S=0.0
IF(I-N) 117,17,117
117 MM=I+1
DO 18 J=MM,N
18 S=S+A(I,J)*X(J)
17 X(I)=(R(I)-S)/A(I,I)
500 RETURN
3  FORMAT (1H , 'MATRIX SINGULAR')
END
```


SUBROUTINE REGEN

SUBROUTINE REGEN

```

C      ****
C      *
C      *          SUBROUTINE REGEN
C      *
C      * THIS SUBROUTINE REGENERATES THE GIVEN DATA AND
C      * CALCULATES THE VARIANCE AND STANDARD DEVIATION OF
C      * THE FIT.
C      *
C      ****

```

```

SUBROUTINE REGEN(X,Y,Z,MM,N)
DIMENSION X(50),Y(50),Z(20)
WRITE(6,1)
1 FORMAT(///,29X,'REGENERATED DATA'//10X,'X MEASURED',5X
1,'Y OBSERVED',5X,'Y CALCULATED',3X,'PCT ERROR',/)
VAR=0.
HI=0.
DO 2 I=1,N
CAL=0.
DO 3 J=1,MM
3 CAL=CAL+Z(J)*X(I)**(J-1)
CAT=ABS(Y(I)-CAL)
PCE=CAT/Y(I)*100.
VAR=VAR+CAT**2
IF(HI-PCE)4,4,2
4 HI=PCE
2 WRITE(6,5) X(I),Y(I),CAL,PCE
5 FORMAT( 9X,4(F10.3,5X)/)
VAR=VAR/(N-1)
DEV=VAR**0.5
WRITE(6,6) VAR,DEV,HI
6 FORMAT(//,10X'VARIANCE' =',F10.6//10X,
1'STANDARD DEVIATION =',F10.6//10X,
2'MAXIMUM PCT ERROR =',F10.6)
RETURN
END

```


SUBROUTINE POLYT

SUBROUTINE POLYT

```

C      ****
C      *
C      *          SUBROUTINE POLYT
C      *
C      * POLYT SUPPLIES REGENERATED DATA AT POINTS INTER-
C      * MEDIATE TO THE GIVEN DATA.
C      *
C      ****

      SUBROUTINE POLYT(X,Z,N,MM)
      DIMENSION X(50),Z(20)
      WRITE(6,1)
1  FORMAT('1',///,32X,'PLOT TEST DATA'//25X'X CALCULATED'
*,4X
1,'Y CALCULATED'/)
      XMAX=0.
      XMIN=99999.
      DO 2 I=1,N
      IF(XMAX-X(I)) 3,3,4
3  XMAX=X(I)
4  IF(X(I)-XMIN) 5,5,2
5  XMIN=X(I)
2  CONTINUE
      DELX=(XMAX-XMIN)/20.
      XY=XMIN
      DO 6 I=1,20
      CAL=0.
      DO15 J=1,MM
15  CAL=CAL+Z(J)*XY**(J-1)
      WRITE(6,7) XY,CAL
7  FORMAT(24X,2(F10.3,5X))
6  XY=XY+DELX
      RETURN
      END

```


SUBROUTINE GAUSS

SUBROUTINE GAUSS

```

C      ****
C      *
C      *          SUBROUTINE GAUSS
C      *
C      * THE FUNCTION OF THIS SUBROUTINE IS TO SOLVE THE
C      * SET OF EQUATIONS A*X=B USING GAUSSIAN ELIMINATION
C      * AND BACK SUBSTITUTION ROTATING ABOUT THE ELEMENT
C      * OF MAXIMUM MODULUS.
C      *
C      ****

```

```

SUBROUTINE GAUSS (A,R,N,X)
DIMENSION A(20,20),R(20),X(20)
M=N-1
DO 11 J=1,M
  S=0.
  DO 12 I=J,N
    U= ABS(A(I,J))
    IF(U-S) 12,12,112
112  S=U
    L=I
  12 CONTINUE
  IF(L-J) 119,19,119
119  DO 14 I=J,N
    S=A(L,I)
    A(L,I)=A(J,I)
  14  A(J,I)=S
    S=R(L)
    R(L)=R(J)
    R(J)=S
  19  IF( ABS(A(J,J))-1.E-30) 115,115,15
115  WRITE(6,3)
    GO TO 500
  15  MM=J+1
    DO 11 I=MM,N
      IF( ABS(A(I,J))-1.E-30) 11,111,111
111  S=A(J,J)/A(I,J)
    A(I,J)=0.0
    DO 16 K=MM,N
      16  A(I,K)=A(J,K)-S*A(I,K)
      R(I)=R(J)-S*R(I)
  11  CONTINUE
    DO 17 K=1,N
      I=N+1-K
      S=0.0
      IF(I-N) 117,17,117
117  MM=I+1
    DO 18 J=MM,N

```


SUBROUTINE GAUSS ... (CONT'D)

```
18 S=S+A(I,J)*X(J)
17 X(I)=(R(I)-S)/A(I,I)
500 RETURN
3  FORMAT (1H , 'MATRIX SINGULAR')
END
```


APPENDIX B

GAS CHROMATOGRAPH CALIBRATION

The gas chromatograph was calibrated using volumetrically prepared samples. The equipment used for sample preparation is illustrated in Figure B.1. Basically it consisted of a 5 liter lucite cylinder, equipped with a moveable piston, and a gas burette. The Lucite cylinder had been calibrated so that the piston position determined the volume of gas it contained.

The cylinder was initially completely purged with N_2 . The known volume of N_2 in the cylinder was then allowed to equilibrate to atmospheric pressure and temperature. The gas burette was then purged with the calibration gas and a volume of the gas brought to atmospheric pressure by means of a mercury reservoir system. The condition of equilibrium was observed by a water manometer. Then a volume of the gas was forced into the Lucite cylinder using the mercury reservoir to maintain a sufficient head. The residual volume of calibration gas was brought to atmospheric condition and the volume recorded. The sample was then mixed for at least 1 hour using a fan built into the lucite cylinder.

Taking into account the pressure, temperature, and specific molar volumes, the sample composition was calculated as mole percent.

A sample mixed in this manner provided more than a sufficient amount to calibrate the gas chromatograph. After the lines had been purged with the gas mixture, the sample loop in the chromatograph was filled to a pressure of 1 inch of mercury. This sample was then injected into the chromatograph He carrier stream and the resulting peak areas measured. Each mixture was run a number of times at varying

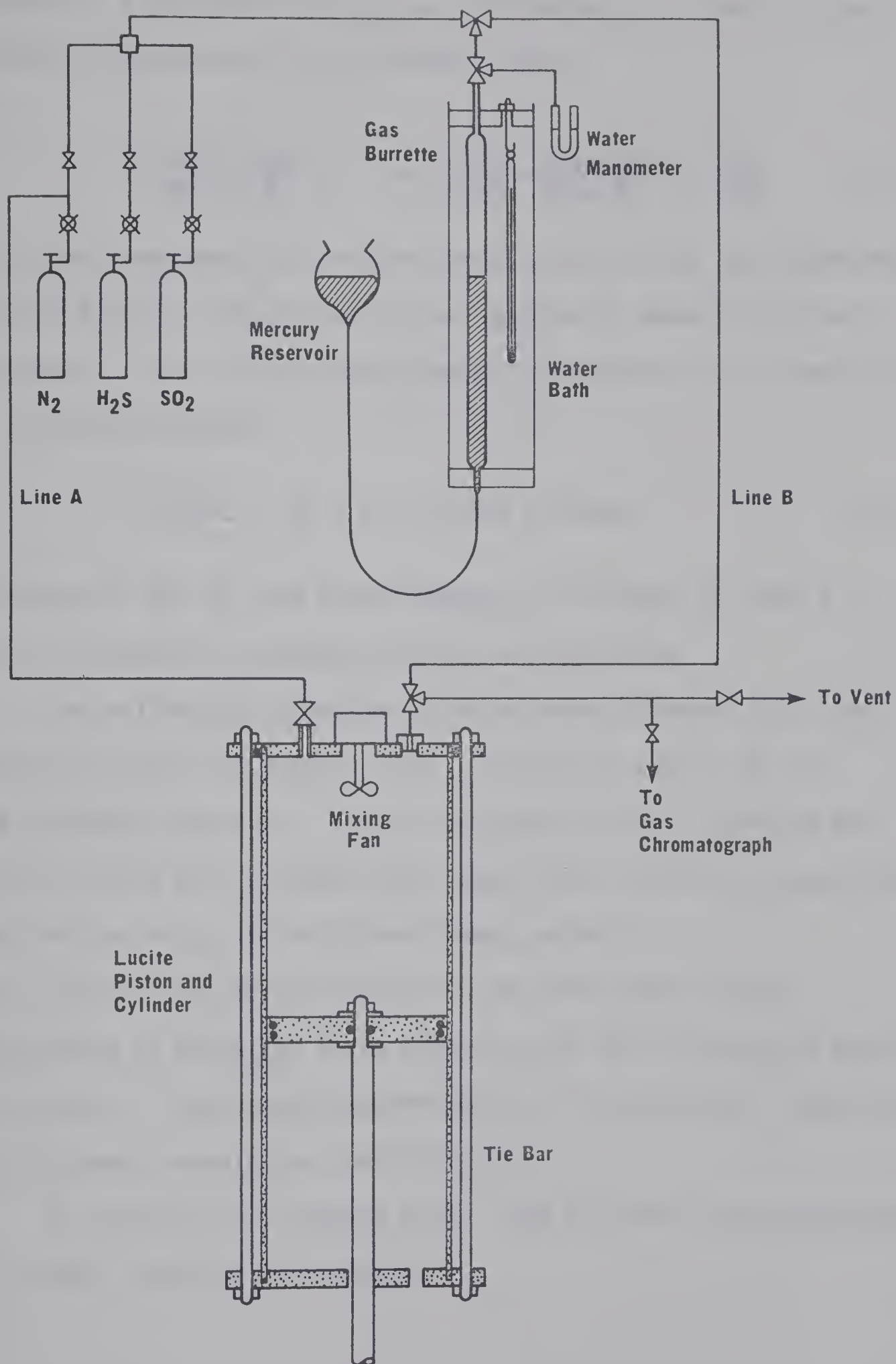


FIGURE B-1: G.C. CALIBRATION EQUIPMENT

attenuations. A calibration curve was constructed on a type of internal standard calculation of the following form:

$$\left(\frac{\text{mole \% gas}}{\text{mole \% N}_2} \right) = a_1 \left(\frac{\text{corr. area gas}}{\text{corr. area N}_2} \right) + \frac{a_0}{100} \quad (\text{B.1})$$

The corrected areas were the measured areas multiplied by the appropriate attenuation factor. The attenuation was applied by means of 10 turn potentiometers. The 10 turn potentiometers were found to be correlated by the following equation

$$\text{ATTEN} = 56 - 5.5 \times (\text{dial setting}) \quad (\text{B.2})$$

A calibration of the 10 turn potentiometers is included as Table B.1. The data and calibration results for SO_2 and H_2S follow.

The calibration equations obtained were different than those obtained by Liu (31) and McGregor (34). This was a result of the revised attenuator equation. The incorrectness of their equation was observed by noting the following facts about their calibration equations:

1. Their values of a_0 did not approximately equal 0.
2. Their values of a_1 were dependent on the attenuator setting.

The combination of these two facts suggests that their attenuator equation was not correct. Experimental determination of the attenuator equation lead to different correlation coefficients.

A listing of the program GCCAL, used to reduce the calibration data to usable results, is included.

TABLE B.1

ATTENUATOR SETTINGS FOR BECKMAN PROGRAMMER

X=ATTENUATOR SETTING
Y=AMPLIFICATION

THE COEFFICIENTS OF THE POLYNOMIAL ARE

A0 = 56.01169

A1 = -5.50067

REGENERATED DATA

X MEASURED	Y OBSERVED	Y CALCULATED	PCT ERROR
10.000	1.000	1.004	0.489
9.800	2.095	2.105	0.479
9.600	3.206	3.205	0.025
9.400	4.313	4.305	0.178
9.000	6.529	6.505	0.358
8.500	9.298	9.255	0.452
8.000	12.065	12.006	0.486
10.000	1.000	1.004	0.489
9.800	2.081	2.105	1.155
9.600	3.157	3.205	1.526
9.400	4.249	4.305	1.325
9.000	6.427	6.505	1.222
8.500	9.144	9.255	1.223
8.000	11.858	12.006	1.250

10.000	1.019	1.004	1.383
9.800	2.130	2.105	1.171
9.600	3.252	3.205	1.439
9.400	4.247	4.305	1.372
9.000	6.583	6.505	1.176
8.500	9.375	9.255	1.270
8.000	12.147	12.006	1.158
10.000	1.017	1.004	1.189
9.800	2.101	2.105	0.192
9.600	3.201	3.205	0.130
9.400	4.286	4.305	0.450
9.000	6.648	6.505	2.142
8.500	9.205	9.255	0.553
8.000	11.921	12.006	0.715

VARIANCE = 0.004808

STANDARD DEVIATION = 0.069342

MAXIMUM PCT ERROR = 2.142339

TABLE B.2

SO2 CALIBRATION EQUATION

X=100*AREA RATIO
Y=100*MOLAR RATIO

THE COEFFICIENTS OF THE POLYNOMIAL ARE

A0 = 0.05186

A1 = 0.74922

REGENERATED DATA

X MEASURED	Y OBSERVED	Y CALCULATED	PCT ERROR
1.110	0.850	0.883	3.941
2.280	1.810	1.760	2.756
3.460	2.690	2.644	1.702
4.860	3.700	3.693	0.186
6.980	5.170	5.281	2.156
12.020	9.100	9.057	0.465

VARIANCE = 0.003996

STANDARD DEVIATION = 0.063220

MAXIMUM PCT ERROR = 3.941957

TABLE B.3

H2S CALIBRATION EQUATION

X=100*AREA RATIO
Y=100*MOLAR RATIO

THE COEFFICIENTS OF THE POLYNOMIAL ARE

A0 = 0.09099

A1 = 0.86043

REGENERATED DATA

X MEASURED	Y OBSERVED	Y CALCULATED	PCT ERROR
0.950	0.870	0.908	4.415
0.940	0.870	0.899	3.426
2.120	1.860	1.915	2.963
2.080	1.860	1.880	1.113
2.080	1.860	1.880	1.113
2.390	2.200	2.147	2.389
2.360	2.200	2.121	3.562
2.350	2.200	2.113	3.953
4.200	3.680	3.704	0.674
4.230	3.680	3.730	1.375
4.140	3.680	3.653	0.728
8.440	7.360	7.353	0.094
8.460	7.360	7.370	0.139
10.030	8.720	8.721	0.013

VARIANCE = 0.002060

STANDARD DEVIATION = 0.045390

MAXIMUM PCT ERROR = 4.415033

MAINLINE GCCAL

MAINLINE GCCAL

```

C *****
C *
C *
C *
C * THIS PROGRAM WAS WRITTEN TO DOCUMENT THE DATA
C * TAKEN FOR THE CALIBRATION OF THE PROCESS GAS
C * CHROMATOGRAPH AND REDUCE THIS DATA TO CALCULATED
C * RESULTS USEFUL FOR THE INTERNAL STANDARD PROCEDURE
C * FOR THE CALIBRATION OF GAS CHROMATOGRAPHS.
C *
C * INPUT DATA
C *
C * NSET - NUMBER OF SETS OF DATA
C * NCOPY - NUMBER OF COPIES OF OUTPUT DESIRED
C * NPAGE - PAGE NUMBER OF FIRST PAGE OF OUTPUT
C * NRUN - CALIBRATION RUN NUMBER
C * NCROM - NUMBER OF CHROMATOGRAMS TAKEN
C * IPEAK - PEAK NUMBER CALIBRATED
C *
C *      ...2 - H2S
C *      ...3 - SO2
C * ICOMP - AREA FLAG
C *
C *      ...1 - COMPUTER AREAS INCLUDED
C *      ...0 - NO COMPUTER AREAS
C *
C * RTEM - ROOM TEMPERATURE (DEG F)
C * APRES - ATMOSPHERIC PRESSURE (MM HG)
C * BTEM - WATER BATH TEMPERATURE (DEG F)
C * V(1) - DISTANCE BETWEEN PISTON AND END OF
C *      CYLINDER (IN)
C *
C * V(2) - VOLUME OF CALIBRATION GAS (CU CM)
C *
C * RDG(1)- AREA OF NITROGEN PEAK
C * RDG(2)- AREA OF CALIBRATION GAS
C * RDG(3)- ATTENUATION FOR NITROGEN
C * RDG(4)- ATTENUATION FOR CALIBRATION GAS
C *
C *      NOTE-NO ATTENUATION=10.0
C *
C *****

```

```

DIMENSION SNAM(4,2),SMV(3),V(2),RDG(7),AVG(7),STORE(40
*,7)
DATA SMV/22403.60,22144.24,21889.30/
DATA SNAM/'HYDR','OGEN','SUL','FIDE','SULF','UR D'
*,'IOXI','DE '/
READ(5,1) NSET,NCOPY
DO 2 ISET=1,NSET
READ(5,1) NRUN,NCROM,IPEAK,ICOMP,NCOMP
READ(5,3) RTEM,BTEM,APRES,V(1),V(2)
IC=1
STEMP=273.
SPRES=760.
RTEM=(RTEM+460.)/1.8

```


MAINLINE GCCAL

...(CONT'D)

BTEM=(BTEM+460.)/1.8

C CALCULATION OF SAMPLE COMPOSITION

C

V(1)=V(1)*2.54

XMN2=(11.+151.192*V(1))*STEMP/RTEM*APRES/SPRES/SMV(1)

V(1)=(11.+151.192*V(1))

XMCAL=V(2)*STEMP/BTEM*APRES/SPRES/SMV(IPEAK)

TOTM=XMN2+XMCAL

XMN2=XMN2/TOTM*100.

XMCAL=XMCAL/TOTM*100.

RMOL=XMCAL/XMN2*100.

KPEAK=IPEAK-1

C READ AND PROCESS PEAK AREA DATA

C

N1=NCROM

N2=1

N3=NCROM+1

N4=NCROM+2

N5=NCROM+3

N6=N4+NCOMP

N7=N6+1

N8=N7+1

NCAT=0

14 DO 4 I=1,7

4 AVG(I)=0.0

DO 5 ICROM=1,NCROM

NCAT=NCAT+1

READ(5,3) RDG

C ADJUSTMENT OF THE AREAS WITH ATTENUATIONS

C

RDG(5)=RDG(2)*(56.-5.5*RDG(4))

RDG(4)=RDG(2)

RDG(2)=RDG(1)*120.

TOTA=RDG(2)+RDG(5)

RDG(3)=RDG(2)/TOTA*100.

RDG(6)=RDG(5)/TOTA*100.

RDG(7)=RDG(5)/RDG(2)*100.

C CALCULATE THE AVERAGES

C

DO 6 I=1,7

6 AVG(I)=RDG(I)+AVG(I)

DO 20 J=1,7

MAINLINE GCCAL

... (CONT'D)

```

20 STORE(NCAT,J)=RDG(J)
  5 CONTINUE
    DO 7 I=1,7
  7  AVG(I)=AVG(I)/NCROM
    NCAT=NCAT+1
    DO 21 J=1,7
21  STORE(NCAT,J)=AVG(J)
    N=NCAT+1
    M=NCAT-1
    DO 29 I=1,2
29  STORE(N,I)=0.

```

C CALCULATE THE VARIANCE AND THE STANDARD DEVIATION
C

```

    DO 30 I=N2,M
30  STORE(N,1)=(STORE(NCAT,7)-STORE(I,7))**2.+STORE(N,1)
    NCAT=NCAT+1
    STORE(NCAT,1)=(STORE(NCAT,1)/M)
    STORE(NCAT,2)=STORE(NCAT,1)**.5
    IF(ICOMP) 9,9,8
  8  ICOMP=0
    N2=N5
    IC=0
    NCROM=NCOMP
    GO TO 14
  9  CONTINUE
    DO 23 IL=1,NCOPY
    WRITE(6,19)
    WRITE(6,10) NRUN,RTEM,BTEM,APRES,V(1),(SNAM(J,KPEAK)
* ,J=1,4),V(2)
    WRITE(6,11) XMN2,(SNAM(J,KPEAK),J=1,4),XMCAL,RMOL
    WRITE(6,12)
    WRITE(6,13) (SNAM(J,KPEAK),J=1,4)
    WRITE(6,15) ((STORE(I,J),J=1,7),I=1,N1)
    WRITE(6,17)
    WRITE(6,15) (STORE(N3,J),J=1,7)
    WRITE(6,18) (STORE(N4,J),J=1,2)
    IF(IC)23,24,23
24  CONTINUE
    WRITE(6,19)
    WRITE(6,10) NRUN,RTEM,BTEM,APRES,V(1),(SNAM(J,KPEAK)
* ,J=1,4),V(2)
    WRITE(6,11) XMN2,(SNAM(J,KPEAK),J=1,4),XMCAL,RMOL
    WRITE(6,16)
    WRITE(6,13) (SNAM(J,KPEAK),J=1,4)
    WRITE(6,40) ((STORE(I,J),J=1,7),I=N5,N6)
    WRITE(6,17)
    WRITE(6,40) (STORE(N7,J),J=1,7)
    WRITE(6,18) (STORE(N8,J),J=1,2)

```


MAINLINE GCCAL

...(CONT'D)

```

23 CONTINUE
  NPAGE=NPAGE+1
2 CONTINUE
1 FORMAT(5I5)
3 FORMAT(7F10.5)
10 FORMAT( /15X,'CALIBRATION SAMPLE NUMBER',I3,///10X
  *, 'SAMPLE PREP
  LARATION CONDITIONS'//12X,'ROOM TEMPERATURE.....'
  *,F7.1,' DEG K
  2',//12X,'BATH TEMPERATURE.....',F7.1,' DEG K',/
  */12X,'ATMOSPHE
  3RIC PRESSURE.....',F7.1,' MM HG',//12X,'VOLUME OF
  * NITROGEN.....
  4.',F7.1,' CC',//12X,'VOLUME OF ',4A4,F7.1,' CC')
11 FORMAT( //,10X,'SAMPLE COMPOSITION (MOLE PERCENT)'/
  */12X,'NITROGEN.
  1.....',F6.2,//12X,4A4,'...',F6.2,//12X,'100X
  * MOLAR RATIO...',
  2F6.2)
12 FORMAT( //,10X,'DISK INTEGRATOR AREA RESULTS',/)
13 FORMAT( 19X,'NITROGEN',13X,4A4,9X,'100X',//11X
  *, 'INPUT',3X,'CORR'
  2,4X,'PCT OF',5X,'INPUT',3X,'CORR',4X,'PCT OF',5X
  *, 'AREA' /11X,'AREA
  3',4X,'AREA',4X,'TOTAL',6X,'AREA',4X,'AREA',4X,'TOTAL'
  *,6X,'RATIO'/)
15 FORMAT(9X,F6.1,2X,F7.1,2X,F6.2,5X,F6.1,2X,F6.1,2X,F6.2
  *,5X,F6.2/)
16 FORMAT( //,10X,'COMPUTER AREA RESULTS',/)
17 FORMAT(/,10X,'AVERAGES')
18 FORMAT(/,50X,'VARIANCE',2X,E10.3,/,50X,'STD. DEV.',1X
  *,E10.3)
19 FORMAT('1',////////)
40 FORMAT(9X,F6.2,2X,F7.2,2X,F6.2,5X,F6.2,2X,F6.2,2X,F6.2
  *,5X,F6.2)
  CALL EXIT
  END

```


APPENDIX C

CALCULATION OF KINETIC RESULTS

C.1 Input Information

The input was entered on request after keyboard queuing the material balance program. A typical input request sequence is included as Table C.1. All entered input was preceded with a ">" and has been underlined for clarity. The input request precedes the input.

C.2 Reduction of Input DataC.2.1 Gas Chromatograph Data

- a) correct areas using attenuation factor.

$$\text{atten factor} = 56 - 5.5 \times (\text{atten setting})$$

$$\text{corr. area} = \text{meas. area} \times \text{atten factor}$$

- b) calculate average areas for each component.

- c) calculate area ratios, $\text{AH}_2\text{S}/\text{AN}_2$ and ASO_2/AN_2 .

- d) calculate molar ratios.

$$\text{MH}_2\text{S}/\text{MN}_2 = 0.86043 \times (\text{AH}_2\text{S}/\text{AN}_2) + 0.9099 \times 10^{-3}$$

$$\text{MSO}_2/\text{MN}_2 = 0.74922 \times (\text{ASO}_2/\text{AN}_2) + 0.5186 \times 10^{-3}$$

- e) calculate mole fractions.

$$\text{FDCOM}_{\text{N}_2} \text{ or } \text{PRCOM}_{\text{N}_2} = 1 / (1 + \text{MH}_2\text{S}/\text{MN}_2 + \text{MSO}_2/\text{MN}_2)$$

$$\text{FDCOM}_{\text{H}_2\text{S}} = \text{FDCOM}_{\text{H}_2\text{S}} \times \text{MH}_2\text{S}/\text{MN}_2$$

$$\text{FDCOM}_{\text{SO}_2} = \text{FDCOM}_{\text{SO}_2} \times \text{MSO}_2/\text{MN}_2$$

C.2.2 H₂O Feeder

- a) $\text{cc/hr} = 0.15581 + 0.52044 \times \text{dial setting}$

- b) $(\text{cc/gm})_T = 1.00597 - 0.00011 \times T_{\text{H}_2\text{O}}$

- c) $\text{gm/hr} = (\text{cc/hr}) / (\text{cc/gm})_T$

TABLE C-1
INPUT REQUEST

DBLK12
 PRELOAD QUEUED OK
 FILE STORAGE FLAG(1-STORE,2-NO)
 JUNCTION FLAG(1-PROC NEW DATA OR 2-PROC FILE DATA)&
 PRINT FLAG(1-TTY,2-NONE
2 1 2
 OF CATALYST(GM)&NUMERIC FILE NO.
5091 50
 UN NO., NO. OF FEED G.C.,NO, OF PROD. G.C.
10-4 2 3 2
 TEMP-REACT. BED,WALL,FLUID BED, PRESS- REACTOR,FEED D/P
13.04 13.04 13.40 17.7 12.2
 SPECIFY H2O FEEDER PCT AND TEMP
12 82
 ATTEN. CODE
2-9.8,2-9.4,3-9.0,4-8.5, 5-10.0
2 5
 FEED G.C. AREAS-N2,H2S,SO2,H2O
12.287 28.641 50.071
12.189 28.464 59.4 345
12.046 28.708 59.244
 SPECIFY ATTEN. CODE--H2S AND SO2
2 5
 PROD. G.C. AREAS
14.081 28.936 56.982
14.021 28.610 57.368

C.2.3 Temperature (°C)

- a) $T_{\text{cat bed}} = 5.3155 + 18.076 \times (\text{M.V.})$
- b) $T_{\text{reactor wall}} = 6.6860 + 17.9544 \times (\text{M.V.})$
- c) $T_{\text{fluid bed}} = 6.3627 + 17.9853 \times (\text{M.V.})$
- d) $T_{\text{reaction}} = (T_{\text{cat bed}} + T_{\text{reactor wall}})/2$

C.2.4 Absolute Pressures

- a) $P_{\text{reactor}} = 716.47 + 6.5452 \times (\text{PCT})$
- b) $P_{\text{feed}} = 22.5 \text{ psia}$

C.2.5 Feed Flow (SCFH)

- a) $FF_{N_2} = -0.0420 + 0.8962 \sqrt{\text{PCT}} + 0.00104 \times (\text{PCT})$
- b) composition correction

$$\rho_{\text{MIX}} = \frac{\sum_{i=1}^3 \text{FDCOM}_i \times \text{MW}_i}{\sum_{i=1}^3 \text{FDMOM}_i \times V_i}$$

		MW	V
i = 1	N ₂	28	22403.60
i = 2	H ₂ S	34	22144.24
i = 3	SO ₂	64	21889.30

$$\rho_{N_2} = 28/V_1$$

$$FF_{\text{MIX}} = FF_{N_2} \times \left(\frac{\rho_{N_2}}{\rho_{\text{MIX}}} \right)^{1/2}$$

C.2.6 Feed Rates (gm.mole/hr)

- a) average molar volume

$$AMV = \left(\sum_{i=1}^3 V_i \times FDCOM_i \right) / 28317.016$$

$$b) \quad FN_2 = (FDCOM_1 \times FF_{MIX}) / AMV$$

$$FH_2S = FN_2 \times (FDCOM_2 / FDCOM_1) \times (V_1 / V_2)$$

$$FSO_2 = FN_2 \times (FDCOM_3 / FDCOM_1) \times (V_1 / V_3)$$

$$FH_2O = (gm \ H_2O / hr) / 18.0588$$

C.2.7 Product Rates (mole/hr)

$$PN_2 = FN_2$$

$$PH_2S = PN_2 \times (PRCOM_2 / PRCOM_1) \times (V_1 / V_2)$$

$$PSO_2 = PN_2 \times (PRCOM_3 / PRCOM_1) \times (V_1 / V_3)$$

$$PH_2O = FH_2O + (FH_2S - PH_2S)$$

$$PS_x = 1.5 \times (FH_2S - PH_2S) / \text{Ave. Mole No. of S}$$

$$PH_2 = (FH_2S - PH_2S) - 2 \times (FSO_2 - PSO_2)$$

C.2.8 Reaction Rates (gm mole/hr/gm.cat)

$$RXH_2S = (FH_2S - PH_2S) / \text{wt of cat.}$$

$$RXSO_2 = (FSO_2 - PSO_2) / \text{wt. of cat.}$$

C.2.9 Conversions (percent)

$$H_2SCN = (FH_2S - PH_2S) \times 100 / FH_2S$$

$$SO_2CN = (FSO_2 - PSO_2) \times 100 / FSO_2$$

C.2.10 WFA

$$WFA = WC / FH_2S$$

C.2.11 Adjust feed composition to allow for H₂O feed

$$FDCOM_i = \frac{F_i}{\sum_{i=1}^4 F_i}$$

C.2.12 Partial Pressures in Reactor (mm Hg)

$$PP_i = \frac{P_i \times P_{\text{reactor}}}{\sum_{i=1}^5 P_i}$$

C.3 Example Calculation for Run 10-4

C.3.1 Gas Chromatograph Data

a)	measured area			corrected area		
	N ₂	H ₂ S	SO ₂	N ₂	H ₂ S	SO ₂
feed	12.287	28.641	59.071	1474.44	123.156	59.071
	12.189	28.464	59.345	1462.68	122.395	59.345
	12.046	28.708	59.244	1445.52	123.444	59.244
			AVE	1460.88	122.998	59.220
prod	14.081	28.936	56.982	1689.72	124.425	56.982
	14.021	28.610	57.368	1682.52	123.724	57.175
			b) AVE	1686.12	123.724	57.175

N₂ atten factor = 120

H₂S atten factor = 56 - 5.5 (9.4) = 4.30

SO₂ atten factor = 56 - 5.5 (10.0) = 1.00

	feed	product
c) AH ₂ S/AN ₂	.084194	.073377
ASO ₂ /AN ₂	.040537	.033909
d) MH ₂ S/MN ₂	.073353	.064044
MSO ₂ /MN ₂	.030890	.025923
e) N ₂	.90560	.91746
H ₂ S	.06642	.05876
SO ₂	.02797	.02378

C.3.2 H₂O Feeder (gm/hr)

- a) $\text{cc/hr} = 0.15581 + 0.52044 (12.0) = 6.40109$
- b) $\text{cc/hr} = 1.00597 - 0.00011 (82) = 0.996950$
- c) $\text{gm/hr} = 6.40109/0.996950 = 6.420673$

C.3.3 Temperatures

- a) $T_{\text{cat bed}} = 5.3155 + 18.076 (13.04) = 241.03$
- b) $T_{\text{wall}} = 6.6860 + 17.9544 (13.04) = 240.81$
- c) $T = (241.03 + 240.81)/2 = 240.92$

C.3.4 Absolute Pressures

- a) $P(\text{reactor}) = 716.47 + 6.5452 (17.70) = 832.32$
- b) $P(\text{feed}) = 22.5 \text{ psia}$

C.3.5 Feed Flow (SCFH)

- a) $\text{FF}_{\text{N}_2} = -0.0420 + 0.8962 \sqrt{12.2} + .00104 (12.2)$
 $= 3.100979$
- b) $\rho_{\text{MIX}} = \frac{.90560 \times 28 + .06643 \times 34 + .02797 \times 64}{.90560 \times 22403.6 + .06643 \times 22144.24 + .02797 \times 21889.3}$
 $= .001314$
- $\rho_{\text{N}_2} = 28/22403.60 = .001249$
- $\text{FF}_{\text{MIX}} = 3.100979 \times (.001249/.001314)^{.5}$
 $= 3.02331$

C.3.6 Feed Rates (gm moles/hour)

- a) average molar volume (ft^3)

$$\text{AMV} = \frac{.90560 \times 22403.6 + .06643 \times 22144.24 + .02797 \times 21889.3}{28317.016}$$

$$= 0.790054$$

$$\begin{aligned}
 \text{b) } \text{FN}_2 &= 0.90560 \times 3.02331 / .790054 = 3.4655 \\
 \text{FH}_2\text{S} &= 0.06643 \times 3.02331 / .790054 = 0.2542 \\
 \text{FSO}_2 &= 0.02797 \times 3.02331 / .790054 = 0.1070 \\
 \text{FH}_2\text{O} &= 6.420673 / 18.0588 = 0.3555
 \end{aligned}$$

C.3.7 Product Rates

$$\begin{aligned}
 \text{PN}_2 &= 3.4655 \\
 \text{PH}_2\text{S} &= 3.4655 \times (.05876 / .91746) \times (\text{VN}_2 / \text{VH}_2\text{S}) \\
 &= 0.2245 \\
 \text{PSO}_2 &= 3.4655 \times (.02378 / .91746) \times (\text{VN}_2 / \text{VSO}_2) \\
 &= 0.0919 \\
 \text{PH}_2\text{O} &= 0.3555 + (.2542 - .2245) = 0.3852 \\
 \text{PS}_x &= 1.5 \times (.2542 - .2245) / 7.34 = 0.0061 \\
 \text{PH}_2 &= (.2542 - .2245) - 2 \times (.1070 - .0919) = -.0005
 \end{aligned}$$

C.3.8 Reaction Rates (gm moles/hr/gm cat.)

$$\begin{aligned}
 \text{RXH}_2\text{S} &= (.2542 - .2245) / .5091 = .05834 \\
 \text{RXSO}_2 &= (.1070 - .0919) / .5091 = .02966
 \end{aligned}$$

C.3.9 Conversions (percent)

$$\begin{aligned}
 \text{H}_2\text{SCN} &= (.2542 - .2245) \times 100 / .2542 = 11.68 \\
 \text{SO}_2\text{CN} &= (.1070 - .0919) \times 100 / .1070 = 14.11
 \end{aligned}$$

C.3.10 WFA

$$\text{WFA} = .5091 / .2542 = 2.003$$

C.3.11 Adjust Feed Composition for H₂O Feed

$$\sum_{i=1}^4 F_i = 4.1822$$

$$N_2 = 100 \times 3.4655/4.1822 = 82.863$$

$$H_2S = 100 \times 0.2542/4.1822 = 6.078$$

$$SO_2 = 100 \times 0.1070/4.1822 = 2.558$$

$$H_2O = 100 \times 0.3555/4.1822 = 8.500$$

C.3.12 Partial Pressures in Reactor (mm Hg)

$$\sum_{i=1}^5 P_i = 4.1732$$

$$N_2 = (3.4655 \times 832.32)/4.1732 = 691.11$$

$$H_2S = (0.2245 \times 832.32)/4.1732 = 44.78$$

$$SO_2 = (0.0919 \times 832.32)/4.1732 = 18.33$$

$$H_2O = (0.3852 \times 832.32)/4.1732 = 76.83$$

$$S_x = (0.0061 \times 832.32)/4.1732 = 1.22$$

TABLE C-2

RAW DATA

RUN	CAT WT.	RED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
10-4	0.5091	13.04	13.04	17.70	12.20	12.0	82.0

	FEED			PROD		
	N2	H2S	SO2	N2	H2S	SO2
ATTEN		9.400	10.000		9.400	10.000
AREA	12.287	28.641	59.071	14.081	28.936	56.962
AREA	12.189	28.464	59.345	14.021	28.610	57.365
AREA	12.046	28.708	59.244			

RUN NUMBER 10-4

UNITS

MASS.....GRAM

PRESSURE.....MILLIMETERS OF MERCURY

TEMPERATURE.....DEGREES KELVIN

TIME.....HOUR

COMPOSITION.....MOLE PERCENT

VOLUME.....STAND. CUBIC FOOT

REACTION RATE...GM MOLES/(HR-GM OF CATALYST

VOLUMETRIC FEED RATE	3.023	WC/FH ₂ S	2.00
REACTION RATE OF H ₂ S	0.0582	REACTION RATE OF SO ₂	0.0296
REACTION TEMPERATURE	513.88	REACTION PRESSURE	832.3
FEED H ₂ S/SO ₂ RATIO	2.3746	PRODUCT H ₂ S/SO ₂ RATIO	2.4421
CONVERSION OF H ₂ S	11.66	CONVERSION OF SO ₂	14.10

MOLECULAR	FEED	PARTIAL PRESSURE	MATERIAL BALANCE	
SPECIE	COMPOSITION	IN REACTOR	FEED	PRODUCT
N ₂	82.86	691.1	3.466	3.466
H ₂ S	6.07	44.7	0.254	0.224
SO ₂	2.55	18.3	0.107	0.091
H ₂ O	8.49	76.8	0.355	0.385
SX	0.00	1.2	0.000	0.006
H ₂	0.00	0.0	0.000	-0.007

AVERAGE NO. OF SULFUR ATOMS/MOLECULE= 7.34

TABLE C-4

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
1-01	0.5091	13.12	13.12	18.00	74.00	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	13.187	37.074	49.739		15.798	38.831	45.369
AREA	13.187	36.921	49.890		15.746	38.609	45.643
AREA					15.704	38.546	45.749

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
1-02	0.5091	13.12	13.12	18.20	73.00	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	12.170	32.771	55.057		14.353	33.558	52.088
AREA	12.186	32.928	54.885		14.432	33.532	52.035

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
1-03	0.5091	13.10	13.10	18.30	73.00	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	9.555	23.369	67.074		11.062	22.588	66.349
AREA	9.572	23.466	66.959		11.018	22.576	66.405

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
2-01	0.5091	13.09	13.09	17.30	32.40	0.0	0.0

		FEED			PROD		
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	11.449	15.247	73.302		13.175	13.220	73.603
AREA	11.520	15.277	73.201		13.150	13.304	73.544

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
2-02	0.5091	13.10	13.10	17.30	65.00	0.0	0.0

		FEED			PROD		
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	11.153	15.631	73.213		12.468	14.162	73.368
AREA	11.112	15.650	73.236		12.475	14.193	73.331

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
2-03	0.5091	13.08	13.08	18.00	12.20	0.0	0.0

		FEED			PROD		
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	6.607	15.458	28.782		13.920	24.350	42.640
AREA	6.629	15.495	28.865		13.690	24.100	41.520
AREA	6.482	15.147	28.481				

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
3-01	0.5091	13.11	13.11	17.30	11.90	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	11.517	15.354	73.128		13.999	12.609	73.390
AREA	11.538	15.417	73.043		14.015	12.495	73.488
AREA	11.545	15.395	73.059		13.980	12.618	73.401

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
3-02	0.5091	13.06	13.06	17.40	23.90	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	11.432	15.132	73.435		13.181	13.054	73.764
AREA	11.421	15.123	73.455		13.197	13.143	73.658
AREA	11.427	15.133	73.439		13.224	13.097	73.677

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
3-03	0.5091	13.06	13.06	17.30	49.90	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	11.440	15.082	73.477		12.759	13.683	73.557
AREA	11.398	15.168	73.433		12.781	13.669	73.548
AREA	11.413	15.100	73.485				

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
3-04	0.5091	13.05	13.05	17.40	79.00	0.0	0.0
		FEED				PROD	
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	6.433	8.483	41.729		6.419	7.089	37.964
AREA	6.430	8.513	41.528		6.406	7.018	37.806
AREA					6.423	7.143	37.643

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
4-01	0.5091	13.12	13.12	19.80	10.20	0.0	0.0
		FEED				PROD	
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		9.400	10.000			9.300	10.000
AREA	13.300	23.530	63.010		14.030	18.340	26.690
AREA	13.630	23.790	62.510		24.030	31.110	43.300

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
4-02	0.5091	13.14	13.14	19.00	9.70	0.0	0.0
		FEED				PROD	
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		9.400	9.800			9.800	9.800
AREA	18.150	31.730	50.100		29.930	32.960	37.100
AREA	18.230	31.820	49.930				
AREA	18.330	31.850	49.800				

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
4-03	0.5091	13.03	13.03	19.00	9.40	0.0	0.0

	N2	FEED H2S	SO2	N2	PROD H2S	SO2
ATTEN		9.400	9.800		9.800	10.000
AREA	16.040	29.890	54.060	10.780	13.960	41.920
AREA	16.130	29.980	53.880	10.800	13.960	41.680

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
4-04	0.5091	13.19	13.19	19.20	9.20	0.0	0.0

	N2	FEED H2S	SO2	N2	PROD H2S	SO2
ATTEN		9.000	10.000		9.400	10.000
AREA	13.780	20.190	66.010	14.360	14.570	24.780
AREA	13.600	20.000	66.110	14.770	14.900	24.890

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
5-01	0.4946	13.17	13.17	19.30	18.00	0.0	0.0

	N2	FEED H2S	SO2	N2	PROD H2S	SO2
ATTEN		9.000	9.800		9.400	9.800
AREA	7.121	7.090	13.480	7.063	8.512	10.192
AREA	7.191	7.418	13.671	7.106	8.493	10.191
AREA	6.984	7.291	13.274	7.081	8.471	10.206

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
5-02	0.4946	13.13	13.13	19.80	18.30	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.000	9.800			9.000	9.800
AREA	6.924	10.521	12.706		6.963	8.269	9.198
AREA	6.969	10.559	13.052		6.927	8.259	9.339
AREA					7.028	8.413	9.270

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
5-03	0.4946	13.12	13.12	20.00	18.00	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		8.500	9.800			8.500	9.800
AREA	6.843	8.607	13.189		6.935	7.295	9.261
AREA	6.895	8.492	13.117		6.888	6.837	9.009
AREA	6.920	8.253	13.040		6.867	7.166	9.073

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
6-01	0.4946	13.08	13.08	19.80	18.20	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.000	9.000			9.400	9.000
AREA	6.822	8.329	10.531		6.931	8.561	9.130
AREA	6.826	8.250	10.656		6.859	8.472	9.172
AREA	6.816	8.324	10.609		6.868	8.524	9.156

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
6-02	0.4946	13.09	13.09	20.00	18.30	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		8.500	9.000			8.500	9.000
AREA	6.502	11.066	10.106		6.587	8.400	8.054
AREA	6.513	10.924	10.185		6.595	8.452	8.075
AREA	6.527	10.970	10.208				

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
6-03	0.4946	13.02	13.02	21.00	17.40	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		8.500	9.800			8.500	10.000
AREA	6.925	8.815	6.686		6.901	7.685	8.240
AREA	6.966	8.944	6.713		6.927	7.745	8.340

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
7-01	0.4946	13.06	13.06	20.00	17.49	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		8.500	9.800			8.500	10.000
AREA	6.931	9.475	7.288		6.911	8.161	7.680
AREA	6.903	9.259	7.057		6.913	8.179	8.282

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
7-02	0.4946	13.07	13.07	20.00	17.70	0.0	0.0
		FEED				PROD	
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		8.500	9.800			8.500	10.000
AREA	6.788	9.239	11.893		6.899	7.371	14.328
AREA	6.797	9.245	11.616		6.847	7.140	14.361
AREA	6.857	9.297	11.897				

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
7-03	0.4946	13.06	13.06	20.00	17.80	0.0	0.0
		FEED				PROD	
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		8.500	9.400			8.500	9.800
AREA	6.771	8.821	10.114		6.831	6.169	14.085
AREA	6.754	8.609	9.996		6.861	6.326	14.353

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
7-04	0.4946	13.06	13.06	20.00	18.00	0.0	0.0
		FEED				PROD	
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		8.500	9.000			8.500	9.400
AREA	6.691	8.662	7.901		6.848	5.777	9.169
AREA	6.704	8.695	8.023		6.850	5.749	9.004

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
7-05	0.4946	13.06	13.06	20.00	18.20	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		8.500	9.000			9.000	9.400
AREA	6.505	8.434	11.465	6.661	7.408	13.586	
AREA	6.530	8.300	11.640	6.665	7.600	13.757	
AREA	6.554	8.289	11.497	6.739	7.652	13.914	

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
7-06	0.4946	13.09	13.09	20.20	17.49	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		8.500	8.500			9.000	9.000
AREA	6.156	10.032	13.002	6.383	8.637	15.252	
AREA	6.184	9.876	12.911	6.331	8.279	15.219	
AREA	6.215	10.010	12.943	6.305	8.294	15.335	

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
8-01	0.4946	13.07	13.07	20.00	17.49	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.000	8.500			9.800	8.500
AREA	6.421	6.667	13.297	6.621	9.877	11.729	
AREA	6.473	7.089	13.132	6.585	9.708	11.834	
AREA				6.577	9.307	11.838	

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
8-02	0.4946	13.07	13.07	20.00	17.30	0.0	0.0

	FEED			PROD		
	N2	H2S	SO2	N2	H2S	SO2
ATTEN		9.000	8.500		9.800	9.000
AREA	6.576	6.448	10.818	6.645	10.820	13.652
AREA	6.587	6.526	10.959	6.690	10.984	13.765

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
8-03	0.4946	13.07	13.07	20.20	17.00	0.0	0.0

	FEED			PROD		
	N2	H2S	SO2	N2	H2S	SO2
ATTEN		9.000	9.400		9.400	9.400
AREA	6.875	6.783	12.888	6.938	6.487	11.361
AREA	6.818	6.684	13.028	6.990	6.661	10.829

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
8-04	0.4946	13.07	13.07	19.60	18.00	0.0	0.0

	FEED			PROD		
	N2	H2S	SO2	N2	H2S	SO2
ATTEN		9.000	9.400		9.400	9.800
AREA	7.039	8.778	7.789	7.066	9.841	12.118
AREA	6.977	8.645	7.842	6.995	9.742	12.243

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
8-05	0.4946	13.11	13.11	20.00	17.70	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.000	9.800			9.000	10.000
AREA	7.113	8.651	8.469		7.127	7.254	12.393
AREA	7.118	8.671	8.628		7.096	7.246	12.291
AREA	7.096	9.055	8.711		7.132	7.270	12.370

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
9-01	0.5091	13.15	13.15	19.00	3.60	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	14.103	26.409	59.487		23.677	25.833	50.488
AREA	14.047	26.319	59.633		23.546	25.049	51.404
AREA	14.200	26.154	59.644		23.399	25.400	51.199

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
9-02	0.5091	13.11	13.11	19.00	3.60	4.0	76.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	14.081	25.833	60.085		8.032	9.762	22.287
AREA	14.182	25.978	59.839		8.812	11.009	23.633
AREA	14.135	25.759	60.105		8.348	10.390	22.901

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
9-03	0.5091	13.10	13.10	19.00	3.20	8.0	76.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	9.800
AREA	14.037	26.419	59.543	10.199	13.676	13.664	
AREA	14.015	26.399	59.584	10.895	14.799	15.067	
AREA	14.160	26.089	59.749				

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
10-1	0.5091	13.06	13.06	18.00	12.20	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	6.488	14.729	29.603	17.052	30.119	52.828	
AREA	6.538	15.105	29.129	17.059	30.322	52.618	

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
10-2	0.5091	13.04	13.04	18.00	12.20	4.0	76.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	6.491	16.586	28.567	6.117	13.301	20.193	
AREA	6.493	16.674	28.925	6.343	13.364	21.490	
AREA	6.504	16.683	28.964	6.348	13.340	21.532	

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
10-3	0.5091	13.04	13.04	18.20	12.20	8.0	81.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	12.047	31.994	55.957		14.552	32.758	52.688
AREA	12.209	31.769	56.021		14.793	32.493	52.713
AREA	12.067	31.881	56.050				

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
10-4	0.5091	13.04	13.04	17.70	12.20	12.0	82.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	12.287	28.641	59.071		14.081	28.936	56.982
AREA	12.189	28.464	59.345		14.021	28.610	57.368
AREA	12.046	28.708	59.244				

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
10-5	0.5091	13.10	13.10	17.80	12.20	16.0	81.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	11.506	27.425	61.066		12.909	27.810	59.280
AREA	11.478	27.517	61.004		5.608	12.195	26.083
AREA	6.531	15.759	35.259		5.703	12.144	25.850

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
11-1	0.5091	13.12	13.12	18.80	12.30	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	9.800			9.400	9.800
AREA	14.671	27.371	57.957	18.073	23.298	58.627	
AREA	14.591	27.396	58.011	18.097	23.025	58.887	
AREA				18.029	23.192	58.777	

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
11-2	0.5091	13.10	13.10	18.30	12.20	4.0	76.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	9.800			9.400	10.000
AREA	14.648	27.064	58.286	10.571	14.864	74.563	
AREA	14.619	27.039	58.340	10.655	14.791	74.552	
AREA	14.653	27.076	58.270				

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
11-3	0.5091	13.12	13.12	18.00	12.30	8.0	81.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	9.800			9.400	9.800
AREA	15.018	27.584	57.397	6.217	9.255	20.736	
AREA	15.094	27.615	57.290	6.189	9.175	20.643	

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
11-4	0.5091	13.10	13.10	17.80	12.30	12.0	81.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	9.800			9.400	9.800
AREA	15.144	27.513	57.341	5.907	9.133	19.979	
AREA	15.055	27.707	57.236	6.079	9.301	20.644	
AREA				5.923	9.294	20.231	

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
11-5	0.5091	13.10	13.10	17.70	12.30	20.0	81.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	9.800			9.400	9.800
AREA	15.060	27.698	57.240	5.711	9.261	19.752	
AREA	15.031	27.705	57.262	5.595	9.027	19.238	
AREA	15.032	27.782	57.185	5.655	9.191	19.462	

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
12-1	0.5091	13.12	13.12	17.70	12.30	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	13.497	25.091	61.411	17.025	24.346	58.604	
AREA	13.492	25.307	61.200	16.997	24.474	58.527	
AREA	13.535	25.100	61.363	17.092	24.325	58.582	

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
12-2	0.5091	13.13	13.13	18.00	12.20	4.0	77.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	13.630	25.082	61.286		6.372	9.683	23.594
AREA	13.544	25.175	61.279		6.409	9.668	23.381
AREA	13.577	25.060	61.362				

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
12-3	0.5091	13.12	13.12	18.00	12.00	8.0	76.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			9.400	10.000
AREA	13.505	25.945	60.548		15.380	25.239	50.379
AREA	13.519	26.037	60.443		15.440	25.295	59.264
AREA	13.419	25.710	60.869		15.202	25.427	59.369

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
13-1	3.8684	13.11	13.11	17.20	8.30	0.0	0.0

	N2	FEED H2S	SO2		N2	PROD H2S	SO2
ATTEN		9.400	10.000			10.000	10.000
AREA	24.284	29.406	46.309		20.158	37.188	0.000
AREA	24.349	29.478	46.180		20.123	36.453	0.000

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
13-2	3.8684	13.11	13.11	17.30	8.40	0.0	0.0
		FEED				PROD	
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		9.400	10.000			10.000	10.000
AREA	20.952	25.219	53.827		6.689	4.478	0.532
AREA	20.927	25.453	53.618		6.720	4.757	0.495
AREA	21.051	25.160	53.787		6.725	4.238	0.723

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
13-3	3.8684	13.05	13.05	17.20	8.30	0.0	0.0
		FEED				PROD	
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		9.400	10.000			10.000	10.000
AREA	16.929	24.274	58.796		6.520	3.358	3.223
AREA	16.800	23.783	59.416		6.516	3.836	2.348

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
13-4	3.8684	13.11	13.11	8.20	1.00	0.0	0.0
		FEED				PROD	
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		9.400	10.000			10.000	10.000
AREA	13.201	18.494	68.303		6.619	1.743	13.377
AREA	13.244	18.405	68.350		6.621	1.635	14.668
AREA					6.621	2.006	12.712

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	RED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
13-5	3.8684	13.13	13.13	18.20	8.10	0.0	0.0

	FEED				PROD		
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		9.400	9.800			10.000	10.000
AREA	13.881	19.220	66.897	8.871	1.865	58.423	
AREA	13.891	19.218	66.889	8.768	1.922	57.884	

RUN	CAT WT.	RED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
14-1	3.8684	13.12	13.12	17.00	4.20	0.0	0.0

	FEED				PROD		
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		9.400	10.000			10.000	10.000
AREA	15.895	26.240	57.863	6.616	6.669	1.507	
AREA	15.899	26.145	57.954	6.648	6.020	1.154	
AREA	15.820	26.253	57.926				

RUN	CAT WT.	RED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
14-2	3.8684	13.14	13.14	17.30	15.30	0.0	0.0

	FEED				PROD		
	N2	H2S	SO2		N2	H2S	SO2
ATTEN		9.400	10.000			10.000	10.000
AREA	16.103	26.178	57.718	6.638	7.546	1.813	
AREA	16.130	25.885	57.984	6.625	7.743	1.820	
AREA	15.848	25.705	58.445	6.643	7.492	1.807	

TABLE C-4 (CONT D)

RAW DATA

RUN	CAT WT.	BED TMP	WALL TMP	REACT PRESS	FEED D/P	PCT	H2O TMP
14-3	3.8684	13.11	13.11	17.20	36.70	0.0	0.0
		FEED			PROD		
		N2	H2S	SO2	N2	H2S	SO2
ATTEN			9.400	10.000		10.000	10.000
AREA	16.203	25.943	57.853		6.642	8.779	2.673
AREA	16.291	25.713	57.994		6.663	8.496	2.934
AREA	16.322	25.884	57.792		6.662	8.667	2.718

TABLE C-5

PROCESSED KINETIC DATA

RUN	CONVERSION		REACTION RATE		REAC. TEMP.	PARTIAL PRESSURE IN THE REACTOR				
	H2S	SO2	SO2	H2S		N2	H2S	SO2	H2O	SX
1-01	11.3	21.0	0.0859	0.1679	515.3	752.6	58.3	14.3	7.4	1.5
1-02	12.4	17.6	0.0847	0.1752	515.3	752.9	55.4	17.8	7.8	1.5
1-03	15.2	12.0	0.0878	0.1929	514.9	748.1	48.4	29.1	8.7	1.7
2-01	22.7	10.1	0.0465	0.1084	514.7	768.2	24.8	27.8	7.3	1.4
2-02	17.7	8.3	0.0559	0.1265	514.9	765.4	27.8	29.1	6.0	1.2
2-03	23.7	27.9	0.0532	0.1185	514.6	760.8	42.3	15.2	13.1	2.0
3-01	31.1	15.0	0.0412	0.0896	515.1	769.1	22.2	26.1	10.0	2.0
3-02	23.6	10.9	0.0432	0.0961	514.2	768.8	24.5	27.8	7.5	1.5
3-03	17.7	8.2	0.0475	0.1048	514.2	767.8	26.3	28.6	5.6	1.1
3-04	15.0	6.7	0.0490	0.1123	514.0	768.0	27.1	29.3	4.8	0.9
4-01	62.3	58.5	0.1099	0.2178	515.3	787.5	16.3	9.6	27.0	5.4
4-02	67.6	52.8	0.1178	0.2263	515.6	779.0	13.7	13.3	28.6	5.7
4-03	64.6	43.1	0.1140	0.2234	513.7	770.6	15.8	19.4	29.0	5.8
4-04	53.1	62.7	0.1138	0.2181	516.5	773.9	25.1	8.8	28.5	5.7
5-01	21.1	21.8	0.0490	0.0908	516.2	787.2	30.1	15.0	8.1	1.6
5-02	20.2	26.0	0.0561	0.1260	515.5	774.1	44.2	14.2	11.2	2.2
5-03	14.9	28.3	0.0616	0.1050	515.3	768.2	53.7	14.0	9.4	1.9
6-01	31.4	12.3	0.0652	0.1508	514.6	757.4	29.9	42.2	13.7	2.7
6-02	23.1	19.5	0.0991	0.2068	514.7	724.6	62.8	37.2	16.0	3.7
6-03	11.5	37.7	0.0423	0.0842	513.5	779.1	59.0	6.3	7.7	1.5
7-01	11.5	43.9	0.0525	0.0889	514.2	769.8	61.7	6.0	8.0	1.6

TABLE C-5 (CONT D)

PROCESSED KINETIC DATA

RUN	CONVERSION		REACTION RATE		REAC. TEMP.	N2	PARTIAL PRESSURE IN THE REACTOR			
	H2S	SO2	SO2	H2S			SO2	H2O	SX	
7-02	21.1	40.3	0.0787	0.1623	514.4	764.2	54.8	10.5	14.7	2.9
7-03	28.0	29.7	0.0995	0.2004	514.2	756.8	47.0	21.4	18.3	3.6
7-04	33.9	24.1	0.0968	0.2423	514.2	750.0	43.0	27.7	22.1	4.4
7-05	36.7	21.0	0.1217	0.2523	514.2	737.5	39.9	42.0	23.2	4.6
7-06	41.1	17.2	0.1513	0.3218	514.7	697.2	44.2	70.1	30.9	6.1
8-01	53.4	10.5	0.0961	0.2066	514.4	729.0	17.1	77.4	19.7	3.9
8-02	44.8	10.5	0.0795	0.1649	514.4	745.2	19.2	64.0	15.6	3.1
8-03	35.0	13.6	0.0580	0.1354	514.4	775.5	23.5	34.3	12.7	2.5
8-04	24.6	21.9	0.0578	0.1255	514.4	778.1	34.5	18.5	11.2	2.2
8-05	16.3	29.0	0.0418	0.0839	515.1	790.3	38.7	9.1	7.5	1.5
9-01	40.6	46.4	0.0465	0.0883	515.8	780.3	27.0	11.2	18.5	3.7
9-02	31.0	33.4	0.0337	0.0664	515.1	734.7	29.0	13.2	61.1	2.6
9-03	26.5	30.2	0.0286	0.0543	514.9	692.1	29.7	13.0	103.7	2.1
10-1	21.4	29.2	0.0573	0.1048	514.2	761.9	42.8	15.4	11.6	2.3
10-2	15.8	22.0	0.0421	0.0859	513.8	731.5	49.2	16.1	35.5	1.8
10-3	14.3	20.1	0.0400	0.0799	513.8	709.5	49.8	16.6	57.8	1.7
10-4	11.6	14.1	0.0296	0.0582	513.8	691.1	44.7	18.3	76.8	1.2
10-5	8.9	11.6	0.0265	0.0452	514.9	670.3	45.6	20.0	96.0	0.9
11-1	30.1	15.8	0.0558	0.1189	515.3	758.8	31.0	33.5	13.4	2.7
11-2	23.1	13.8	0.0489	0.0897	514.9	731.9	32.5	33.2	36.4	1.9
11-3	17.7	10.2	0.0348	0.0686	515.3	710.2	33.5	32.1	56.7	1.4

TABLE C-5 (CONT D)

PROCESSED KINETIC DATA

RUN	CONVERSION		REACTION RATE		REAC. TEMP.	PARTIAL PRESSURE		IN THE REACTOR	
	H ₂ S	SO ₂	SO ₂	H ₂ S		N ₂	H ₂ S	H ₂ O	SX
11-4	14.0	8.2	0.0279	0.0545	514.9	689.2	33.9	31.7	76.8
11-5	10.9	7.2	0.0245	0.0425	514.9	652.0	33.5	30.4	115.4
12-1	21.9	22.0	0.0442	0.0890	515.3	768.2	34.9	17.2	9.8
12-2	16.8	16.3	0.0324	0.0676	515.5	745.5	35.8	17.9	33.5
12-3	12.8	16.0	0.0315	0.0530	515.3	722.7	37.8	17.3	55.1
13-1	62.9	95.7	0.0092	0.0188	515.1	794.3	11.2	0.4	19.1
13-2	84.8	93.4	0.0120	0.0253	515.1	793.4	4.5	0.8	25.6
13-3	59.0	85.4	0.0146	0.0306	514.0	785.0	3.8	2.5	31.3
13-4	93.2	58.3	0.0048	0.0103	515.1	722.5	2.1	9.8	29.6
13-5	94.3	32.9	0.0150	0.0293	515.5	763.4	1.8	32.5	31.3
14-1	84.8	92.2	0.0115	0.0236	515.3	779.0	6.1	1.4	34.2
14-2	81.5	90.1	0.0216	0.0432	515.6	781.7	7.2	1.7	32.4
14-3	79.2	85.9	0.0317	0.0641	515.1	781.4	8.0	2.4	30.8

MAINLINE MAT BAL

MAINLINE MAT BAL

```

C      ****
C      *
C      *
C      *   MATERIAL BALANCE ON THE RECYCLE REACTOR FOR H2S- *
C      *   SO2 REACTION. INPUT IS REQUESTED ON THE TELETYPE *
C      *   IN A FREE FORMAT INPUT STYLE. THE RAW DATA AND THE*
C      *   PROCESSED DATA MAY BE ENTERED IN USER DEFINED DISK*
C      *   FILES BY THE PROGRAM.
C      *
C      ****

```

```

      DEFINE FILE 100 (51,106,U,NEXT),200(51,80,U,NEXT)
      DIMENSION CR(4,6),TEMP(3),PRESS(3),FDCOM(7),PRCOM(7)
*,BAL(
12,7), V(3),T(2,3),P(2,2),DP(3),PCR(4,6),WFLOW(2)
      DATA V/22403.60,22144.24,21889.30/
      DATA T/5.3155,18.0706,6.6860,17.9544,6.3627,17.9853/
      DATA P/15.002,.25101,716.47,6.5452/
      DATA DP/-.0420,.8962,.00104/
      DATA WFLOW/.15581,.52044/
      CALL GETTY(LUNR)
      LUNW=LUNR
      ISTRT=1
      IEND=0.

```

```

C      *** DETERMINE THE DATA SOURCE..TTY(NEW) OR DISK (OLD)

      WRITE(LUNW,121)
121 FORMAT('FILE STORAGE FLAG(1-STORE,2-NO)'/ 'FUNCTION
* FLAG(1-PROC ',
1 'NEW DATA OR 2-PROC FILE DATA)$'/' PRINT FLAG(1-TTY,2
*-NONE')
      CALL FFINP(LUNR,3,0,ISTOR,0,IFUNC,0,IPR,IEROR)
      GO TO(88,33),IFUNC

```

```

C      *** DATA READ FROM DISK FILE

      33 WRITE(LUNW,122)
122 FORMAT('HOW MANY POINTS$,AT WHAT RUN NO. IN THE FILE
* TO START AT')
      CALL FFINP(LUNR,2,0,NUM,0,ISTRT,IEROR)
      ISTRT=ISTRT-1
      IEND=ISTRT+NUM

```


MAINLINE MAT BAL

...(CONT'D)

```

34  ISTRT=ISTR+1
    NFIL=ISTR
    READ (100,NFIL)NFIL,NFDCR,NPRCR,INCOM,WC,RUN,TEMP
    *,PRESS,MFH2S,
    1MFSO2,MPH2S,MPSO2,((CR(I,J),PCR(I,J),I=1,4),J=1,4),DP
    *,WFPCT,WTMP
    WRITE(LUNR,123) ISTR
123  FORMAT('RUN NO.'1X,I3,1X,'FINISHED')
    GO TO 35

```

C *** DATA READ FROM TTY

```

88  WRITE(LUNW,90)
90  FORMAT('WT OF CATALYST(GM)$NUMERIC FILE NO.')
```

CALL FFINP(LUNR,2,1,WC,0,NFIL,IEROR)

WRITE(LUNW,100)

```

100  FORMAT('RUN NO., NO. OF FEED G.C.,NO. OF PROD. G.C.')
```

CALL FFINP(LUNR,3,3,RUN,0,NFDCR,0,NPRCR,IEROR)

INCOM=0

WRITE(LUNW,105)

```

105  FORMAT('TEMP-REACT. BED,WALL,FLUID BED, PRESS- REACTOR
*,FEED D/P')
```

CALL FFINP(LUNW,5,1,TEMP(1),1,TEMP(2),1,TEMP(3),1,

1 PRESS(2),1,PRESS(3),IEROR)

PRESS(1)=30.0

WRITE(LUNR,106)

```

106  FORMAT('SPECIFY H2O FEEDER PCT AND TEMP')
```

CALL FFINP(LUNR,2,1,WFPCT,1,WTMP,IEROR)

WRITE(LUNW,108)

```

108  FORMAT('ATTEN. CODE',/, '1-9.8,2-9.4,3-9.0,4-8.5, 5
*-10.0')
```

CALL FFINP(LUNR,2,0,MFH2S,0,MFSO2,IEROR)

WRITE(LUNW,113)

```

113  FORMAT('FEED G.C. AREAS-N2,H2S,SO2,H2O')
```

DO 116 I=1,NFDCR

```

116  CALL FFINP(LUNR,4,1,CR(I,1),1,CR(I,2),1,CR(I,3),1,CR(I
*,4),IEROR)
```

WRITE(LUNW,109)

```

109  FORMAT('SPECIFY ATTEN. CODE--H2S AND SO2')
```

CALL FFINP(LUNR,2,0,MPH2S,0,MPSO2,IEROR)

WRITE(LUNW,117)

```

117  FORMAT('PROD. G.C. AREAS')
```

DO 120 I=1,NPRCR

```

120  CALL FFINP(LUNR,4,1,PCR(I,1),1,PCR(I,2),1,PCR(I,3),1
*,PCR(I,4),
1IEROR)
```

GO TO (40,35), ISTR

MAINLINE MAT BAL

...(CONT'D)

C *** STORE RAW DATA IN DISK FILE.

```

40 WRITE(100'NFIL')NFIL,NFDCR,NPRCR,INCOM,WC,RUN,TEMP
   *,PRESS,MFH2S,
   1MFSO2,MPH2S,MPSO2,((CR(I,J),PCR(I,J),I=1,4),J=1,4),DP
   *,WFPCT,WTMP
35 CALL CHROM(FDCOM,CR,MFH2S,MFSO2,NFDCR,INCOM)
   CALL CHROM(PRCOM,PCR,MPH2S,MPSO2,NPRCR,INCOM)

```

C *** CALCULATE H2O RATE (CC/HR)

```

WRATE=WFLOW(1)+WFLOW(2)*WFPCT

```

C *** CONVERT TO GM/HR

```

WRATE=WRATE/(1.00597-.00011*WTMP)
IF(WFPCT)23,23,24
23 WRATE=0.
24 CONTINUE

```

C *** CALCULATE TEMPERATURES FROM CALIBRATION COEFFS.

```

DO 14 J=1,3
  TMP=0.
  DO 15 I=1,2
15  TMP=TMP+T(I,J)*TEMP(J)**(I-1)
14  TEMP(J)=TMP

```

C *** CALCULATE ABS PRESSURES FROM CALIBRATION COEFFS.

```

J=2
PRS=0.
DO 17 I=1,2
17  PRS=PRS+P(I,J)*PRESS(J)**(I-1)
PRESS(2)=PRS
PRESS(1)=22.5

```

C *** CALCULATE FLOW RATE

```

PRESS(3)=PRESS(3)**0.5
FDP=0
DO 19 I=1,3
19  FDP=FDP+DP(I)*PRESS(3)**(I-1)

```


MAINLINE MAT BAL

...(CONT'D)

PRESS(3)=FDP

C *** FLOW RATE COMPOSITION CORRECTION

```

ROMIX=(28.*FDCOM(1)+34.*FDCOM(2)+64.*FDCOM(3))
*/(FDCOM(1)*V(1)+FDCOM(2)*V(2)+FDCOM(3)*V(3))
PRESS(3)=PRESS(3)*(28./V(1)/ROMIX)**0.5

```

C *** CALCULATE MATERIAL BALANCE

C *** SUMV=AVG. MOLAR VOL. OF THE FEED GAS.

```

SUMV=(FDCOM(1)*V(1)+FDCOM(2)*V(2)+FDCOM(3)*V(3))
*/28317.016

```

C *** FEED FLOW FOR N2,H2S,SO2

```

DO 10 J=1,3
10 BAL(1,J)=FDCOM(J)*PRESS(3)/SUMV

```

C *** FEED FLOW FOR H2O

BAL(1,4)=WRATE/18.0588

C *** PRODUCT FLOWS FOR N2,H2S,SO2,H2O,ATOMIC S, AND H2

```

BAL(2,1)=BAL(1,1)
BAL(2,2)=BAL(2,1)*(PRCOM(2)*V(1)/PRCOM(1)/V(2))
BAL(2,3)=BAL(2,1)*(PRCOM(3)*V(1)/PRCOM(1)/V(3))
BAL(2,4)=BAL(1,4)+BAL(1,2)-BAL(2,2)
BAL(2,5)=3*(BAL(1,2)-BAL(2,2))/2.
BAL(2,6)=BAL(1,2)-BAL(2,2)-2*(BAL(1,3)-BAL(2,3))

```

C *** CALCULATE AVERAGE MOLECULAR WEIGHT OF SULFUR

```

PRS=PRESS(2)/760.*BAL(2,5)/8.
RTEMP=(TEMP(1)+TEMP(2))/2.+273.
22 CALL FREM(PRS,RTEMP,XS)
PRS1=PRESS(2)/760.*BAL(2,5)/XS
IF(ABS((PRS-PRS1)/PRS1)-0.005) 20,20,21

```


MAINLINE MAT BAL

... (CONT'D)

```

21 PRS=PRS1
   GO TO 22
20 BAL(2,5)=BAL(2,5)/XS

```

C *** CALCULATE REACTION RATES

```

RXH2S=(BAL(1,2)-BAL(2,2))/WC
RXSO2=(BAL(1,3)-BAL(2,3))/WC

```

C *** CALCULATE FEED AND PRODUCT H2S/SO2 RATIOS

```

FDRAT=BAL(1,2)/BAL(1,3)
PRRAT=BAL(2,2)/BAL(2,3)

```

C *** CALCULATE CONVERSION OF H2S AND SO2

```

H2SCN=(BAL(1,2)-BAL(2,2))/BAL(1,2)*100.
SO2CN=(BAL(1,3)-BAL(2,3))/BAL(1,3)*100.
WFA=WC/BAL(1,2)

```

C *** ADJUST FEED COMP. TO ALLOW FOR AUX. H2O FEED

```

TOT=0.
DO 9 J=1,4
9 TOT=TOT+BAL(1,J)
DO 11 J=1,4
11 FDCOM(J)=BAL(1,J)/TOT*100.

```

C *** CALCULATE PARTIAL PRESSURES IN REACTOR

```

TOT=0.
DO 12 J=1,5
12 TOT=TOT+BAL(2,J)
DO 13 J=1,5
13 PRCOM(J)=BAL(2,J)*PRESS(2)/TOT

```

C *** DATA OUTPUT

```

GO TO (43,44), IPR

```

C *** TTY OUTPUT

```

43 CALL OUTPT(RUN,PRESS,RXH2S,RXSO2,RTEMP,FDRAT,PRRAT

```


MAINLINE MAT BAL

...(CONT'D)

```
* ,H2SCN,SO2CN  
1   ,FDCOM,PRCOM,BAL,LUNW,WFA,XS,IPR)  
44 GO TO (41,42), ISTR
```

C *** FILE OUTPUT

```
41 WRITE(200'NFIL) H2SCN,WFA,RUN,RTEMP,FDRAT,PRESS(2)  
   * ,PRESS(3),RXH2S,  
   1 RXSO2,SO2CN,PRRAT,XS,FDCOM,PRCOM,BAL  
42 IF(ISTR-IEND)34,65,65  
65 CALL EXIT  
   END
```


SUBROUTINE CHROM

SUBROUTINE CHROM

```

C      ****
C      *
C      *          CHROM
C      *
C      *
C      * CHROM CALCULATES STREAM COMPOSITIONS FROM THE
C      * CHROMATOGRAPHIC AREA RESULTS USING THE CALIBRATION *
C      * COEFFICIENTS DETERMINED USING THE INTERNAL STANDARD*
C      * PROCEDURE
C      *
C      ****

```

```

SUBROUTINE CHROM(COMP,CR,MH2S,MSO2,N,INCOM)
DIMENSION COMP(7),CR(4,6),ATTEN(6),HSN2(2),SON2(2)
*,A(5)
DATA SON2/.05186,.74922/, HSN2/.09099,.86043/
DATA A/9.8,9.4,9.0,8.5,10./
ATTEN(1)=120.
ATTEN(2)=56.-5.5*A(MH2S)
ATTEN(3)=56.-5.5*A(MSO2)
ATTEN(4)=1.
ATTEN(5)=1.
ATTEN(6)=1.
XN=N
DO 1 J=1,6
CR(4,J)=0.
DO 1 I=1,N
1 CR(4,J)=CR(4,J)+CR(I,J)*ATTEN(J)/XN
HNRAT=HSN2(1)/100.+HSN2(2)*CR(4,2)/CR(4,1)
SNRAT=SON2(1)/100.+SON2(2)*CR(4,3)/CR(4,1)
COMP(1)=1./(1.+HNRAT+SNRAT)
COMP(2)=HNRAT*COMP(1)
COMP(3)=1.-COMP(1)-COMP(2)
RETURN
END

```


APPENDIX D

DATA HANDLING

The raw and processed data were stored in user defined disk files by the data processing coreload. The data were then available to various off-line coreloads for the following purposes

1. punching data on cards
2. restoring data from cards to the files
3. displaying data

MAINLINE PDATA

MAINLINE PDATA

```

C      *****
C      *
C      *
C      *   PUNCH DATA FROM EITHER OF THE DATA FILES.
C      *
C      *****

```

```

      DEFINE FILE 100(51,106,U,NEXT)
      DEFINE FILE 200(51,80,U,NEXT)
      DIMENSION PRESS(3),TEMP(3),CR(4,6),PCR(4,6),DP(3)
      DIMENSION VAR(40)
      DATA IAST/'*'/
      LUNW=9
      LUNR=LUNW
      WRITE(LUNW,100)
      3 WRITE(LUNW,110)
110  FORMAT('1-RAW FILE, 2-PROC. FILE')
      CALL FFINP(LUNR,1,0,IFL,IEROR)
      WRITE(LUNR,104)
104  FORMAT('HOW MANY BLOCKS IN THIS FILE')
      CALL FFINP(LUNR,1,0,NBLOC,IEROR)
      DO 50 IL=1,NBLOC
      WRITE(LUNW,105) IL
      CALL FFINP(LUNR,2,0,ISTRT, 0,IEND,IEROR)
      GO TO (1,2),IFL
      1 DO 40 NREC=ISTRT,IEND
      NUM=6
      READ (100,NREC)NFIL,NFDCR,NPRCR,INCOM,WC,RUN,TEMP
      *,PRESS,MFH2S,
      1MFSO2,MPH2S,MPSO2,((CR(I,J),PCR(I,J),I=1,4),J=1,4),DP
      *,WFPCT,WTMP
      CALL CHECK
      WRITE(5,200) RUN,WC,TEMP,PRESS
      CALL CHECK
      WRITE(5,201) NFDCR,NPRCR,INCOM,MFH2S,MFSO2,MPH2S,MPSO2
      IF(INCOM-0)20,20,21
20  NUM=4
21  CONTINUE
      DO 22 L=1,NFDCR
      CALL CHECK
22  WRITE(5,202) (CR(L,M),M=1,NUM)
      DO 23 L=1,NPRCR
      CALL CHECK
23  WRITE(5,202) (PCR(L,M),M=1,NUM)
      CALL CHECK
      WRITE(5,101) DP,WFPCT,WTMP

```


MAINLINE PDATA

... (CONT'D)

```
40 CONTINUE
   GO TO 50
   2 DO 11 NFIL=ISTRT,IEND
     READ(200,NFIL) VAR
     CALL CHECK
     WRITE(5,102) VAR(3)
102  FORMAT(A4)
     CALL CHECK
     WRITE(5,101) VAR(1),VAR(2),(VAR(J),J=4,9)
     CALL CHECK
     WRITE(5,101) (VAR(J),J=10,17)
     CALL CHECK
     WRITE(5,101) (VAR(J),J=18,25)
     CALL CHECK
     WRITE(5,101) (VAR(J),J=26,33)
     CALL CHECK
   11 WRITE(5,101) (VAR(J),J=34,40)
50  CONTINUE
100  FORMAT('PUNCH OUT DATA FILES')
101  FORMAT(8F10.5)
105  FORMAT('BLOCK',I3,/, 'STARTING RECORD$ LAST RECORD')
200  FORMAT(A4,4X,F6.4,4X,6F6.2)
201  FORMAT(7I5)
202  FORMAT(6F8.5)
   14 READ(5,103) I
103  FORMAT(A1)
     IF(I-IAST)13,9,13
   13 CALL STACK
     GO TO 14
   9  WRITE(LUNR,106)
106  FORMAT('1-CONTINUE, 2-EXIT')
     CALL FFINP(LUNR,1,0,IDEC,IEROR)
     GO TO (3,12),IDEC
   12 CALL EXIT
     END
```


SUBROUTINE CHECK

SUBROUTINE CHECK

```

C      ****
C      *
C      *
C      *   PUNCH STATION CHECKED FOR BLANK CARDS.
C      *
C      ****

```

```

SUBROUTINE CHECK
DIMENSION CHAR(20)
DATA BLANK/' '/
14 READ(5,99) CHAR
99 FORMAT(20A4)
DO 12 ID=1,20
  IF(CHAR(ID)-BLANK)11,12,11
12 CONTINUE
13 RETURN
11 WRITE(1,98)
98 FORMAT('NONBLANK CARD IN PUNCH**PUSH START TO RESUME
* EXECUTION')
PAUSE
GO TO 14
END

```


MAINLINE RAWRD

MAINLINE RAWRD

```

C      *****
C      *
C      *
C      *   READ DATA FROM CARDS INTO RAW DATA FILE.
C      *
C      *****

```

```

      DEFINE FILE 100(51,106,U,NEXT)
      DIMENSION PRESS(3),TEMP(3),CR(4,6),PCR(4,6),DP(3)
      LUNR=9
      LUNW=9
      WRITE(LUNW,100)
100  FORMAT('READ IN RAW DATA')
      WRITE(LUNW,101)
101  FORMAT('HOW MANY BLOCKS OF RECORDS')
      CALL FFINP(LUNR,1,0,NBLOC,IEROR)
      DO 50 IL=1,NBLOC
      WRITE(LUNW,102) IL
102  FORMAT('BLOCK',I3,/, 'STARTING RECORD$ LAST RECORD')
      CALL FFINP(LUNR,2,0,ISTRT, 0,IEND,IEROR)
      DO 40 IJ=ISTRT,IEND
      DO 19 I=1,4
      DO 19 J=1,4
      CR(I,J)=0.
19  PCR(I,J)=0.
      NFIL=IJ
      NUM=6
      READ(5,200) RUN,WC,TEMP,PRESS
200  FORMAT(A4,4X,F6.4,4X,6F6.2)
      READ(5,201) NFDCCR,NPRCR,INCOM,MFH2S,MFSO2,MPH2S,MPSO2
201  FORMAT(7I5)
      IF(INCOM-0)20,20,21
20  NUM=4
21  CONTINUE
      DO 22 L=1,NFDCCR
22  READ(5,202) (CR(L,M),M=1,NUM)
      DO 23 L=1,NPRCR
23  READ(5,202) (PCR(L,M),M=1,NUM)
202  FORMAT(6F8.3)
      READ(5,203) DP,WFPCT,WTMP
203  FORMAT(8F10.5)
      WRITE(100'IJ)NFIL,NFDCCR,NPRCR,INCOM,WC,RUN,TEMP,PRESS
      *,MFH2S,
      1MFSO2,MPH2S,MPSO2,((CR(I,J),PCR(I,J),I=1,4),J=1,4),DP
      *,WFPCT,WTMP
40  CONTINUE

```


MAINLINE RAWRD

... (CONT'D)

```
50 CONTINUE
60 CALL EXIT
END
```


MAINLINE PRORD

MAINLINE PRORD

```

C *****
C *
C *   READ DATA FROM CARDS INTO THE PROC. DATA FILE.   *
C *
C *****

```

```

      DEFINE FILE 200(51,80,U,NEXT)
      DIMENSION VAR(40)
  9  READ(5,100) ISTRT,IEND
100  FORMAT(2I5)
      IF(ISTRT)12,12,10
 10  DO 11 NFIL=ISTRT,IEND
      READ(5,102) VAR(3)
102  FORMAT(A4)
      READ(5,101) VAR(1),VAR(2),(VAR(J),J=4,40)
101  FORMAT(8F10.5)
 11  WRITE(200,NFIL) VAR
      GO TO 9
 12  CALL EXIT
      END

```


MAINLINE OUT

MAINLINE OUT

```

C *****
C *
C *
C *   DISPLAY OF PROCESSED DATA RECORDS ON PRINTER OR *
C *   ANY TELETYPE. *
C *
C *****

```

```

      DEFINE FILE 200(51,80,U,NEXT)
      DIMENSION FDCOM(7),PRCOM(7),BAL(2,7),PRESS(3)
      CALL GETTY(LUNR)
      WRITE(LUNR,110)
110  FORMAT('SPECIFY OUTPUT DEVICE')
      CALL FFINP(LUNR,1,0,LUNW,IEROR)
      IPR=3
      WRITE(LUNR,100)
100  FORMAT('OUTPUT OF PROC. DATA DISK FILE')
      WRITE(LUNR,101)
101  FORMAT('HOW MANY BLOCKS OF RECORDS')
      CALL FFINP(LUNR,1,0,NBLOC,IEROR)
      DO 40 I=1,NBLOC
      WRITE(LUNR,102) I
102  FORMAT('HOW MANY RECORDS IN BLOCK ',I3)
      CALL FFINP(LUNR,1,0,NUM,IEROR)
      WRITE(LUNR,103)
103  FORMAT('WHERE DOES IT START')
      CALL FFINP(LUNR,1,0,ISTR,IEROR)
      IEND=ISTR+NUM-1
      DO 30 J=ISTR,IEND
      NFIL=J
      READ(200,NFIL) H2SCN,WFA,RUN,RTEMP,FDRAT,PRESS(2)
      *,PRESS(3),RXH2S,
      1 RXSO2,SO2CN,PRRAT,XS,FDCOM,PRCOM,BAL
      CALL OUTPT(RUN,PRESS,RXH2S,RXSO2,RTEMP,FDRAT,PRRAT
      *,H2SCN,SO2CN
      1 ,FDCOM,PRCOM,BAL,LUNW,WFA,XS,IPR)
      30 CONTINUE
      40 CONTINUE
      WRITE(6,300)
300  FORMAT('1')
      CALL EXIT
      END

```


SUBROUTINE OUTPUT

SUBROUTINE OUTPUT

```

      SUBROUTINE OUTPT(RUN,PRESS,RXH2S,RXSO2,RTEMP,FDRAT
      *,PRRAT,H2SCN,
1   SO2CN,FDCOM,PRCOM,BAL,LUNW,WFA,XS,IPR)
      DIMENSION PRESS(3),PRCOM(7),FDCOM(7),BAL(2,7)
      LUNR=LUNW
      IF(IPR-1)14,14,15
15  LUNW=6
14  WRITE(LUNW,5)
      5  FORMAT('1')
      WRITE(LUNW,1) RUN
      1  FORMAT(////10X,'RUN NUMBER',1X,A4)
      IF(LUNW-6)11,11,12
11  WRITE(LUNW,10)
10  FORMAT(/37X,'UNITS'//18X,'MASS.....GRAM'/)
      WRITE(LUNW,9)
      9  FORMAT( 18X,'PRESSURE.....MILLIMETERS OF MERCURY' /
      */18X,'TEMPER
      1ATURE.....DEGREES KELVIN'//18X,'TIME.....HOURL' /
      */18X,'COMPOS
      1ITION.....MOLE PERCENT'//18X,'VOLUME.....STAND.
      * CUBIC FOOT')
      WRITE(LUNW,8)
      8  FORMAT(/,18X,'REACTION RATE...GM MOLES/(HR-GM OF
      * CATALYST'///)
12  WRITE(LUNW,3) PRESS(3),WFA
      3  FORMAT(10X,'VOLUMETRIC FEED RATE',F7.3,5X,'WC/FH2S'
      *,14X,F7.2/)
      WRITE(LUNW,2) RXH2S,RXSO2,RTEMP,PRESS(2)
      2  FORMAT(10X,'REACTION RATE OF H2S',F7.4,5X , 'REACTION
      * RATE OF SO2
      1'F7.4//10X,'REACTION TEMPERATURE',F7.2,5X , 'REACTION
      * PRESSURE
      1'F7.1/)
      WRITE(LUNW,6) FDRAT,PRRAT,H2SCN,SO2CN
      6  FORMAT(10X,'FEED H2S/SO2 RATIO ' ,F7.4,5X , 'PRODUCT
      * H2S/SO2 RATI
      10',F7.4//10X,'CONVERSION OF H2S ' ,F7.2,5X
      *, 'CONVERSION OF SO2
      1 ' ,F7.2,///)
      WRITE(LUNW,4) (FDCOM(J),PRCOM(J),BAL(1,J),BAL(2,J)
      *,J=1,6)
      4  FORMAT(10X,'MOLECULAR',5X,'FEED',6X,'PARTIAL PRESSURE'
      *,4X,'MATERIA
      1L BALANCE'//11X,'SPECIE',4X'COMPOSITION',4X,'IN
      * REACTOR',8X,'FEED
      1 PRODUCT'//13X,'N2 ' ,7X,F6.2,9X,F6.1,9X,F7.3,3X
      *,F7.3//13X,'H2S'
      1,7X,F6.2,9X,F6.1,9X,F7.3,3X,F7.3//13X,'SO2',7X,F6.2,9X
      *,F6.1,9X,F7.

```


SUBROUTINE OUTPUT

...(CONT'D)

```
13,3X,F7.3//13X,'H2O',7X,F6.2,9X,F6.1,9X,F7.3,3X,F7.3/  
*/13X,'SX ',7X  
1,F6.2,9X,F6.1,9X,2(F7.3,3X)//13X'H2'8X,F6.2,9X,F6.1,9X  
*,2(F7.3,3X))  
WRITE(LUNW,7) XS  
7 FORMAT(////,13X,'AVERAGE NO. OF SULFUR ATOMS/MOLECULE=  
* 'F6.2)  
IF (IPR-2)13,16,13  
16 LUNW=LUNR  
IPR=3  
GO TO 12  
13 RETURN  
END
```


MAINLINE DPLOT

MAINLINE DPLOT

```

C *****
C *
C *
C *   PLOTS FROM PROCESSED DATA FILE
C *
C *****

```

```

      DEFINE FILE 200(51,80,U,NEXT)
      DIMENSION X(50),Y(50),IY(7),IX(7),VAR(23),LX(4,4)
      *,LY(10,7),LABX(40
      1),NLY(7),PH2S(50),PSO2(50),PH2O(50),LABY(40)
      COMMON X,Y,N,XMAX,XMIN,YMAX,YMIN,RTEMP,FDRAT,RUN1,RUN2
      *,LABX,NLABX,
      1LABY,NLABY,IDEC,PH2S,PSO2,PH2O,INDY
      DATA NLY/9,9,9,9,1,10,6/,IY/1,10,8,9,4,5,21/,IX/2,21
      *,22,23/
      DATALY/'H','2','S',' ',' ','C','O','N','V',' ','S','O'
      *,'2',' ','C'
      1,'O','N','V',2*' ','1','O','O','O','*','R','H','2','S'
      *,' ','S','O'
      2,'2',' ','R','A','T','E',' ',' ','K',9*' ','F','E','E'
      *,'D',' '
      3'R','A','T','I','O','P','H','2','S',6*' '/'
      DATA LX/' ','W','F','A','P','H','2','S','P','S','O'
      *,'2','P','H',
      1'2','O'/

```

C** GETTY WILL DETERMINE WHICH TELETYPE IS BEING USED.

```

      CALL GETTY(LUNR)
      LUNW=LUNR
      9 CONTINUE
      IDEC=2
      WRITE(LUNW,103)
      103 FORMAT(' WHERE DO YOU WANT THE PLOT,1-SCOPE$0
      *-PLOTTER')
      CALL FFINP(LUNR,1,0,ID,IEROR)
      CALL SCALF(1.,1.,0.,0.)

```

C** PLOTD SETS UP EITHER THE PLOTTER OR THE SCOPE

```

      CALL PLOTD(ID)
      IF(ID)12,12,11
      11 CONTINUE

```


MAINLINE DPL0T

... (CONT'D)

```

CALL ERASE
CALL ORGSC(0.,0.)
12 CONTINUE
SUMT=0.
SUMFD=0.

```

C** DETERMINE THE ORDINATE VARIABLE

```

WRITE(LUNR,100)
100 FORMAT('SPECIFY VARIABLE FOR VERTICAL',/,'1-H2S CONV',
*/,
1'2-SO2 CONV',/,'3-H2S RATE*1000',/,'4-SO2 RATE*1000',/
*,'5-F(PH2S,'
1'PSO2,RH2S)'/,'6-FEED RATIO',/,'7-PH2S')
CALL FFINP(LUNR,1,0,1,IEROR)
IF(I-3)4,3,4
3 WRITE(LUNR,105)
105 FORMAT('DO YOU WISH TO GENERATE POINTS',/,'1-YES 2
*-NO')
CALL FFINP(LUNR,1,0,1DEC,IEROR)
4 CONTINUE

```

C** SET UP THE ORDINATE LABEL

```

DO 1 J=1,25
1 LABY(J)=LY(J,I)
NLABY=NLV(I)

```

C** INDY DETERMINES THE POSITION IN THE FILE OF THE
C** IVARIABLE

```

INDY=IY(I)

```

C** DETERMINE ORDINATE MIN. AND MAX.

```

WRITE(LUNR,104)
CALL FFINP(LUNR,2,1,YMIN,1,YMAX,IEROR)

```

C** DETERMINE INFORMATION FOR THE ABSCISSA

```

WRITE(LUNR,101)
101 FORMAT('SPECIFY VARIABLE FOR HORIZ.',/,'1-WFA',/,'2
*-PH2S',/,'
1'3-PSO2',/,'4-PH2O')
CALL FFINP(LUNR,1,0,1,IEROR)

```


MAINLINE DPLOT

... (CONT'D)

```

      DO 2 J=1,4
2     LABX(J)=LX(J,I)
      NLABX=4
      INDX=IX(I)
      WRITE(LUNR,104)
104    FORMAT('SPECIFY MIN. AND MAX. FOR AXIS')
      CALL FFINP(LUNR,2,1,XMIN,1,XMAX,IEROR)

C**   VALUES OF VAR FROM THE FILE
C       VAR(1) H2S CONVERSION
C       (2) WFA (FEED H2S RATE/WT. OF CAT.)
C       (3) RUN ALPHANUMERIC
C       (5) FEED H2S/SO2 RATIO
C       (8) H2S RATE
C       (9) SO2 RATE
C       (10) SO2 CONVERSION
C       (11) PROD. RATIO
C       (21) PH2S
C       (22) PSO2
C       (23) PH2O

C**   DETERMINE LOCATION OF DATA IN FILE

      N=0
      I=0
      WRITE(LUNR,106)
106    FORMAT(' HOW MANY BLOCKS OF DATA')
      CALL FFINP(LUNR,1,0,NBLK,IEROR)
      DO 15 J=1,NBLK
      WRITE(LUNW,102)
102    FORMAT('STARTING RECORD, LAST RECORD')
      CALL FFINP(LUNR,2,0,ISTRT,0,IEND,IEROR)
      IF(J-1)13,13,14
13     READ(200,ISTRT) VAR
      RUN1=VAR(3)
14     DO 10 IJ=ISTRT,IEND
      NFIL=IJ
      I=I+1
      READ(200,NFIL) VAR
      VAR(2)=VAR(21)*VAR(22)**.5

C**   VAR(4) SET TO F(PH2S,PSO2,H2S RATE)

      VAR(4)=VAR(21)*VAR(22)**.5/VAR(8)

```


MAINLINE DPL0T

...(CONT'D)

C** REACTION RATES MULT. BY 1000 FOR PURPOSES OF SCALING

```
VAR(9)=VAR(9)*1000.
VAR(8)=VAR(8)*1000.
Y(I)=VAR(INDY)
X(I)=VAR(INDX)
PH2S(I)=VAR(21)
PSO2(I)=VAR(22)
PH2O(I)=VAR(23)
SUMFD=SUMFD+VAR(5)
SUMT=SUMT+VAR(4)
10 CONTINUE
15 N=IEND-ISTRT+1+N
RTEMP=SUMT/N
FDRAT=SUMFD/N
RUN2=VAR(3)
WRITE(LUNR,203)
203 FORMAT('HOW MANY COPIES')
CALL FFINP(LUNR,1,0,NCOP,IEROR)
DO 20 I=1,NCOP
20 CALL BKPLT
WRITE(LUNW,202)
202 FORMAT(/,'0-EXITS 1-PLOT AGAIN')
CALL FFINP(LUNR,1,0,NPLT,IEROR)
IF(NPLT) 50,50,9
50 CONTINUE
CALL EXIT
END
```


SUBROUTINE BKPLT

SUBROUTINE BKPLT

```

C      ****
C      *
C      *
C      *   PLOTTING OF POINTS.
C      *
C      ****

```

```

SUBROUTINE BKPLT
  DIMENSION LABX(40),LABY(40),ITITL(4,60),NTITL(4)
  DIMENSION X(50),Y(50),PH2S(50),PSO2(50),PH2O(50)
  COMMON X,Y,N,XMAX,XMIN,YMAX,YMIN,RTEMP,FDRAT,RUN1,RUN2
  *,LABX,NLABX,
  1LABY,NLABY,IDEC,PH2S,PSO2,PH2O,INDY
  FUNC(PA,PB,PC)=B1*(PA**B2)*(PB**B3)
  B1=.0005547
  B2=.92916
  B3=.76004

```

```

C**  FUNC IS USED TO GENERATE POINTS
C**  SET UP VARIABLES FOR THE GENERAL PLOTTING ROUTINE PLOT1

```

```

      DO 121 I=1,4
121  NTITL(I)=0
      NX=10
      NY=20
      XL=6.8
      XS=.2
      YS=.2
      ANG=0.
      NTPX=2
      INCX=2
      INCY=2
      CALL PLOT1(LABX,NLABX,LABY,NLABY,ITITL,NTITL,XMAX,XMIN
  *,YMAX,YMIN,
  1NX,NY,XL,XE,YE,NTPX,INCX,INCY)

```

```

C**  PLOT POINTS WITH CHARACTER DETERMINED BY ICHAR

```

```

      ICHAR=1
      DO 13 I=1,N
        XP=X(I)
        YP=Y(I)
        CALL FPLOT(-2,XP,YP)
        CALL POINT (ICHR)

```


SUBROUTINE BKPLT

...(CONT'D)

```
13 CALL FPLLOT(1,XP,YP)
   GO TO (9,11),IDEC
9 ICHAR=2
```

C** GENERATE POINTS

```
DO 10 I=1,N
  XF=X(I)
  YF=FUNC(PH2S(I),PSO2(I),PH2O(I))*1000.
  CALL FPLLOT(-2,XF,YF)
  CALL POINT(ICHR)
10 CALL FPLLOT(1,XF,YF)
```

C** INDY=4 INDICATES LINEAR FORM OF RATE EQUATION REQUIRED

```
11 IF(INDY-4)70,61,70
61 YN=1./0.000861
   XN=0.
   CALL FPLLOT(-2,XN,YN)
   XN=XMAX
   YN=0.00874*XMAX/0.000861+YN
   IF(YN-YMAX)63,63,62
62 XN=0.000861/0.00874*YMAX-1./0.861
   YN=YMAX
63 CALL FPLLOT(-1,XN,YN)
```

C** RETURN TO PLOT ORIGIN FOR SPACING TO NEXT PLOT

```
70 CALL FPLLOT(0,XMIN,YMIN)
   CALL SCALF(1.,1.,0.,0.)
   CALL FCHAR(.7,-1.2,.2,.2,0.)
   WRITE(7,112) RUN1,RUN2
112 FORMAT('RUNS ',A4,' TO ',A4)
   CALL FPLLOT(-2,1.4,-1.4)
   CALL POINT(0)
   CALL FPLLOT(1,1.6,-1.4)
   CALL FCHAR(1.6,-1.4,.1,.1,0.)
   WRITE(7,115)
115 FORMAT('EXPERIMENTAL POINTS')
   GO TO (12,60),IDEC
12 CALL FPLLOT(-2,1.4,-1.6)
   CALL POINT(2)
   CALL FPLLOT(1,1.6,-1.6)
   WRITE(7,116)
116 FORMAT('GENERATED POINTS')
60 CALL FPLLOT(0,6.8,-3.1)
   CALL SCALF(1.,1.,0.,0.)
   RETURN
```


SUBROUTINE PLOT1

SUBROUTINE PLOT1

```

C      ****
C      *
C      *
C      *   GENERATION OF AXIS, LABELLING OF AXIS AND TITLING*
C      *   OF PLOT                                           *
C      *   X AXIS IS THE AXIS DOWN THE LENGTH OF THE PAPER. *
C      *   Y AXIS IS THE AXIS ACROSS THE WIDTH OF THE PAPER. *
C      ****

```

```

      SUBROUTINE PLOT1(LABX,NLABX,LABY,NLABY,TITLE,NTITL
* ,XMAX,XMIN,YMAX,
1 YMIN,NX,NY,XL,XEND,YEND,NTYPX,INCX,INCY)
      INTEGER TITLE(4,60)
      DIMENSION LABX(40),LABY(40),NTITL(4)
      THT=3.1416/2.
      UX=(XMAX-XMIN)/NX+.0000001
      UY=(YMAX-YMIN)/NY+.0000001
      CALL FPLLOT(-2,.5,.5)
      CALL POINT(0)

```

```

C      *****DECIDE IF VERTICAL OR HORIZONTAL PLOT

```

```

      IF(NX-NY)16,16,15

```

```

C      ***** HORIZONTAL

```

```

15  YN=3.5
     SX=XL/NX
     SY=4./NY
     XN=2.7+(7.8-XL)/2.
     YL=4.
     GO TO 17

```

```

C      *****VERTICAL

```

```

16  XN=3.2
     YL=XL
     XL=4.8
     YN=3.0+(7.0-YL)/2.
     SX=4.8/NX
     SY=YL/NY

```


SUBROUTINE PLOT1

...(CONT'D)

17 CALL FPLLOT(1,XN,YN)

C ***** STORE INFORMATION TO SPACE AFTER PLOT

```

XEND=XN
YEND=-YN
XN= SX * NX
YN= SY * NY
CALL SCALF(1.,1.,0.,0.)

```

C ***** GENERATE AXES

```

CALL FGRID(0,0.,0.,SX,NX)
CALL FGRID(1,XN,0.,SY,NY)
CALL FGRID(2,XN,YN,SX,NX)
CALL FGRID(3,0.,YN,SY,NY)
NX=NX+1
NY=NY+1
X=XMIN
Y=YMIN
IF(NTYPX) 25,24,25

```

C ***** NTYPX=0 DEFAULTS TO NTYPX=1, INCX=1

```

24 INCX=1
   INCY=1
   NTYPX=1
25 CONTINUE

```

C ***** ANNOTATE HORIZONTAL AXIS

GO TO (26,27),NTYPX

C ***** NTYPX=1, VERTICAL ANNOTATION ON HORIZ, AXIS

```

26 XN=0.
   YN=-.85

```

C ***** NX=NUMBER OF DIVISIONS

C ***** INCX=LABEL EVERY N TH POINT

C ***** UX=DISTANCE BETWEEN DIVISIONS IN PLOT UNITS

```

DO 20 I=1,NX,INCX
CALL FCHAR(XN,YN,.10,.15,THT)
WRITE(7,100) X

```


SUBROUTINE PLOT1

...(CONT'D)

```

      X=X+UX*INCX
20  XN=XN+SX*INCX
100 FORMAT(F8.1)
      YN=-1.05
      GO TO 40
27  XN=-.35

```

C ***** NTYPX=2, HORIZON, ANNOTATION ON HORIZON. AXIS

```

      YN=-.30
      DO 28 I=1,NX,INCX
      CALL FCHAR(XN,YN,.1,.15,0.)
      WRITE(7,102) X
102 FORMAT(F5.1)
      X=X+UX*INCX
28  XN=XN+SX*INCX
      YN=-.6

```

C ***** LABEL HORIZON. AXIS

```

40  XN=(XL-NLABX*.15)/2.
      CALL FCHAR(XN,YN,.15,.15,0.)
      WRITE(7,101) (LABX(I),I=1,NLABX)
101 FORMAT(40A1)
      YN=-1.4

```

C ***** INSCRIBE PLOT TITLES

```

      DO 23 I=1,4
      IF(NTITL(I))23,23,22
22  XN=(XL-NTITL(I)*.15)/2.
      CALL FCHAR(XN,YN,.15,.15,0.)
      N=NTITL(I)
      WRITE(7,103) (TITLE(I,J),J=1,N)
23  YN=YN-.2
103 FORMAT(60A1)

```

C ***** ANNOTATE VERTICAL AXIS

```

      XN=-.85
      YN=0.
      DO 21 I=1,NY,INCY
      CALL FCHAR(XN,YN,.10,.15,0.)
      WRITE(7,100) Y
      Y=Y+UY*INCY
21  YN=YN+SY*INCY

```


SUBROUTINE PLOT1

...(CONT'D)

C ***** LABEL VERTICAL AXIS

YN=(YL-NLABY*.15)/2.

XN=-1.05

CALL FCHAR(XN,YN,.15,.15,THT)

WRITE(7,101) (LABY(I),I=1,NLABY)

C ***** SCALE PLOT

CALL FPLLOT(0,0.,0.)

UX= SX/UX

UY= SY/UY

CALL SCALF(UX,UY,XMIN,YMIN)

RETURN

END

APPENDIX E

GAS CHROMATOGRAPH JOB DEFINITION

E.1 Parameters

A more descriptive presentation of the job definition has been presented elsewhere (17). Only the variable parameters of interest to this project were reviewed below.

The job definition parameters were divided into four categories as follows:

1. general information
2. time band information
3. parameter action times
4. ECO action times

E.1.1 General

The job definition included the specification of the following general parameters:

- a) number of allowed peaks
- b) time band in which reference peak will occur
- c) finish time of the chromatogram
- d) number of time bands
- e) number of parameter and ECO actions

E.1.2 Time Bands

The job was further specified by the optional definition of time bands to allow peak identification. Each time band defined required the following information:

- a) time band start and finish
- b) peak separation method to be used for any fused

peaks occurring in this time band

- c) alphanumeric name to be associated with the areas integrated in this time band.

E.1.3 Parameter Actions

One set of parameter cards was required for each action.

This card specified the following:

- a) type of time used, relative or absolute
- b) action time
- c) new values of the following parameters
 - (i) status
 - (ii) rate of scan
 - (iii) dead band
 - (iv) number of repeats for "hard" decision
 - (v) number of repeats for "soft" decision
 - (vi) exponential filter factors for the two derivatives

A discussion of selecting the numerical values for these scan parameters was presented in section 5.12.

E.1.4 ECO Actions

Each ECO action required an ECO parameter card including the following information:

- a) ECO contact address to be acted on
- b) time of action
- c) action, i.e. open or closed

E.2 Entering a Job Definition

Once the parameters were punched on cards according to the

format specified (17), they were entered into a permanent disk file by executing the GCMTN coreload. Once these parameters had been accepted by the GCMTN coreload the teletyped queued coreload GCJOB was executed to initialize the following:

1. G.C. number
2. report teletype
3. report calculation option
4. job definition number

Now each time that the interrupt associated with this particular gas chromatograph was closed, a scan was carried out using the parameters specified in the job definition. The job definition to be used could be changed to any defined job by executing GCJOB when the particular gas chromatograph was idle.

The job definition for the N_2 , H_2S , SO_2 , H_2O analysis on a 4 foot x 1/8 inch Chromosorb 104 column and a 6 foot x 1/8 inch Porapak Q-S column is included as Table E.1. Table E.2 is the GCJOB portion of the definition.

TABLE E-1

E-4

12 JAN 72
13/51 HRS

** GAS CHROMATOGRAPH JOB LISTING **

JOB NUMBER = 15 CALCULATION OPTION = 7
GC NUMBER = 1 TOTAL PEAKS = 7

FINISH TIME = 300
NORMALIZATION CONST. = 100.

& REFERENCE PEAK DATA *

LOW TIME OF REF PEAK 5.
HIGH TIME OF REF PEAK 55.
CONCENTRATION OF REF PEAK 0.
RESPONSE FACTOR OF REF PEAK 0.

* TIME BAND DATA *

LOW TIME	HIGH TIME	CONC FOR	STND	FACTOR	JTYPE	COMPONENT
15.	35.	0.		1.	1	N2
60.	120.	0.		1.	1	H2S
150.	230.	0.		1.	1	SO2
240.	280.	0.		1.	1	H2O

COMPONENT	SEQNO	IPLUS	INREF	IFCGO	IREST	UNITS
N2	1	0	9	0	0	(
H2S	2	0	0	0	0	(
SO2	3	0	0	0	0	(
H2O	4	0	0	0	0	(

* PARAMETER AND CONTROL ACTION DATA *

PARAMETER ACTIONS

ACTION TIME	KNDTM	ISTS	IRATE	IHIGH	ILOW	IHARD	ISOFT	IEXP1	IEXP2
0	AB	11	8PPS	15	-15	7	6	1	2
5	AB	1	8PPS	30	-30	7	6	1	2
30	RL	0	4PPS	30	-30	9	8	1	1
125	RL	0	2PPS	30	-30	7	6	1	1
210	RL	0	1PPS	30	-99	4	3	1	1
300	RL	19	1PPS	30	-99	4	3	1	1

ECO ACTIONS

NO ECO ACTIONS SPECIFIED

JOB COMPLETE

// END 12 JAN 72 13.52.08

TABLE E-2

>QGCJOB
CORELOAD QUEUED OK
12 JAN 72
14/ 3 HRS

** GAS CHROM. JOB ENTRY **

ENTER G.C. NUMBER, JOB NUMBER, REPORT LUN AND KALC

>1 15 12 7

G.C. NUMBER = 1

JOB NUMBER = 15

OUTPUT LUN = 12

KALC OPTION = 7

TYPE 1 IF OK ... 2 IF NOT

>1

JOB ENTERED

APPENDIX F
PROGRAMS DEVELOPED IN THIS PROJECT FOR USE WITH THE
GAS CHROMATOGRAPH PACKAGE

A facility was available to obtain digitized results from one chromatograph at a constant scan rate of 16 points per second. These results were then used for picking the scan parameters or producing plots.

During this special run all other chromatographs were locked out of the system. The special system was initiated by keyboard queuing RAWLD. Then the job entry coreload, GCJOB, was queued and job number 99 specified. Once these two steps had been completed the package was activated by the usual interrupt. The data was stored for 10 minutes or until the interrupt was closed a second time.

Once the data acquisition was complete the data were available to the off-line coreloads. As well a hard copy in the form of a punched deck was available through the IBM system function *DUMP.

The coreloads available were as follows:

- 1) TEST - calculate derivatives at various scan rates to aid in specification of scan parameters.
- 2) DATPT - plot of the following
 - a) signal
 - b) first derivative
 - c) second derivative

Used as an aid to selecting scan parameters.

- 3) GCPLT - plot of the signal. This provided more flexibility and more options than the above plot routine.

MAINLINE TEST

MAINLINE TEST

```

C      *****
C      *
C      *
C      *   PROCESSING OF DATA STORED BY RAWGC TO CALCULATE *
C      *   THE FIRST AND SECOND DERIVATIVES IN THE SAME WAY *
C      *   AS THE G.C. SCAN ROUTINE. *
C      *
C      * INPUT *
C      *   NUM-FIRST RECORD IN THE FILE(TIME*16 IN THE SCAN) *
C      *   IEND-LAST RECORD IN THE FILE *
C      *   TITLE-RUN NAME *
C      *   ISCAN-SCAN RATE INDICATOR *
C      *       0-16 PPS *
C      *       1-08 *
C      *       2-04 *
C      *       3-02 *
C      *       4-01 *
C      *       5-1/2 *
C      *       6-1/4 *
C      *   IEX1-FIRST DER. EXPONENTIAL FILTER FACTOR *
C      *
C      *   IEX2-SECOND DER. EXPONENTIAL FILTER FACTOR *
C      *   THIS SEQUENCE IS REPEATED FOR AS MANY CASES AS *
C      *   DESIRED. THE PROGRAM WILL END ON A BLANK CARD. *
C      *
C      *****

```

```

      INTEGER Y(13),DYDX1,DYDX2,DYEX1,DYEX2
      DIMENSION TITLE(20),SCORE(19)
      DATA SCORE/19*'-----'/
      DEFINE FILE 100( 9600,1,U,NEXT)
20  READ(5,500) NUM,IEND
      IF(IEND)101,101,21
21  TOTAL=0.
      READ(5,504) TITLE
504  FORMAT(20A4)
      READ(5,500) ISCAN,IEX1,IEX2
      INCR=2**ISCAN
      SCAN=16./INCR
      IEND=IEND+7*INCR
      NFIL=NUM-7*INCR
      NUM=NUM-INCR
      IF(NFIL)18,19,19
18  NFIL=0
      NUM=NFIL+7*INCR
19  WRITE(6,505) TITLE,SCAN,IEX1,IEX2

```


MAINLINE TEST

...(CONT'D)

```

500 FORMAT(3I5)
505 FORMAT('1',////////,33X,'G.C. DATA ANALYSIS',////////,20X
*,20A4,///,33X,
1 'SCAN RATE',F6.2,///,33X,'FIRST DERIVATIVE FILTER
* CONSTANT',3X,I2
2,/,33X,'SECOND DERIVATIVE FILTER CONSTANT',2X,I2)
LAST=0
DO 4 I=1,12
NFIL=NFIL+INCR
IF(NFIL-IEND)3,3,100
3 CONTINUE
READ(100'NFIL) Y(I)
IF(Y(I))101,4,4
4 LAST=LAST+Y(I)

```

C ***** CALCULATE THE AVERAGE AREA UNDER THE BASE LINE

```

LAST=LAST/12
5 WRITE(6,507)
507 FORMAT('1',///)
WRITE(6,506) SCORE
WRITE(6,502)
502 FORMAT(50X,'DERIVATIVES',/,39X,'UNSMOOTHED',14X
*, 'SMOOTHED'
1,5X,'INCREMENTAL',/,14X,'TIME',5X,'SIGNAL',6X,'FIRST'
*,6X,
2 'SECOND',6X,'FIRST',6X,'SECOND',4X,'AREA')
WRITE(6,506) SCORE
506 FORMAT(13X,19A4)
DO 8 IJ=1,50
NFIL=NFIL+INCR
IF(NFIL-IEND)9,9,100
9 READ(100'NFIL) Y(13)

```

C ***** SUM IS THE INDIVIDUAL INCREMENT THAT EACH POINT ADDS
C ***** TO TOTAL

```

SUM=Y(7)-LAST
SUM=SUM*INCR

```

C ***** TOTAL IS THE TOTAL AREA OF THE PEAK LESS THE BASE
C ***** LINE CORRECTIO

```

TOTAL=TOTAL+SUM

```

C ***** BRANCH OUT ON A NEGATIVE POINT

```

IF(Y(13)) 101,6,6
6 NUM=NUM+INCR

```


MAINLINE TEST

...(CONT'D)

```
C  **** DYDX1 IS THE UNSMOOTHED FIRST DERIVATIVE, DYEX1 THE
C  ***SMOOTHED

      CALL DER1(Y,DYDX1,DYEX1,IEX1)

C  **** DYDX2 IS THE UNSMOOTHED SECOND DERIVATIVE, DYEX2 THE
C  ***SMOOTHED

      CALL DER2(Y,DYDX2,DYEX2,IEX2)
      WRITE(6,501) NUM,Y(7),DYDX1,DYDX2,DYEX1,DYEX2,SUM
501  FORMAT(5X,6(5X,I6),7X,F8.0)

C  **** SHIFT THE POINTS BACK ONE IN PREPARATION FOR THE
C  ***NEXT POINT

      DO 7 I=1,12
      7 Y(I)=Y(I+1)
      8 CONTINUE
      GO TO 5
100  CONTINUE
      WRITE(6,503) TOTAL
503  FORMAT(///,13X,'TOTAL AREA= ',E13.4)
      GO TO 20
101  WRITE(6,503) TOTAL
      CALL EXIT
      END
```


SUBROUTINE DER1

SUBROUTINE DER1

```

C      *****
C      *
C      *
C      *   CALCULATION OF FIRST DERIVATIVE BY A LEAST SQ.
C      *   APPROX. TECHNIQUE OUTLINED BY SAVITXKY AND GOLAY
C      *   ANAL. CHEM. ,VOL 36. P1627 (JULY 1964).
C      *
C      *****

```

```

SUBROUTINE DER1(Y,DYDX1,DYEX1,IEX1)
INTEGER Y(13),DYDX1,DYEX1,DLAST
DATA DLAST/0/
DYDX1=(Y(10)-Y(4)+Y(9)-Y(5))*2.
DYDX1=DYDX1+Y(10)-Y(4)+Y(8)-Y(6)
DYEX1=(DYDX1+DLAST)/2**IEX1
DLAST=DYDX1
RETURN
END

```


SUBROUTINE DER2

SUBROUTINE DER2

SUBROUTINE DER2 (Y,DYDX2,DYEX2,IEX2)

INTEGER Y(13),DYDX2,DYEX2,DLAST

DATA DLAST/0/

 $DYDX2 = (Y(13) + Y(1) - 2*Y(7) + Y(12) - Y(6) + Y(2) - Y(8)) * 2.$ $DYDX2 = DYDX2 + Y(13) + Y(1) - 2*Y(7)$ $DYDX2 = DYDX2 + Y(3) - Y(5) - Y(9) + Y(11)$ $DYEX2 = (DYDX2 + DLAST) / 2 * IEX2$

DLAST=DYDX2

RETURN

END

MAINLINE GCPLT

MAINLINE GCPLT

```

C      *****
C      *
C      *
C      *   PROGRAM TO PLOT G.C. DATA FROM RAWLD FILES
C      *
C      *****

```

```

      INTEGER TITLE(2,60)
      DIMENSION NX(6),NXL(6),TX(6), INCX(6),NTITL(2)
      *,INCXL(6)
      DIMENSION IY(3),LAB(60)
      DATA NX/15,15,4*14/,INCX/3*1,2,4,8/,TX/90.,180.,420.,
1 840.,1680.,3360./,INCXL/10,5,4*2/
      DATA NXL/1,3,7,14,28,56/
      DEFINE FILE 100(9600,1,U,NEXT)
1 READ(5,100) ITYPE,NCOPY,ID

```

```

C**  ITYPE-SPECIFIES LENGTH OF TIME CHROMATOGRAM COVERS
C**      1-1.5 MIN.
C**      2-3
C**      3-7
C**      4-14
C**  NCOPY-NOT USED
C**  ID-SPECIFIES PLOT DEVICE
C**      0-PLOTTER
C**      1-SCOPE

```

```

      CALL SCALF(1.,1.,0.,0.)
      IF(ITYPE)80,80,2
100 FORMAT(3I3)
      2 IF(ID)9,9,8
      8 CALL PLOTD(ID)
      CALL ERASE
      CALL ORGSC(0.,0.)
      9 DO 10 I=1,2
10 READ(5,101) (TITLE(I,J),J=1,60),NTITL(I)

```

```

C**  TITLE-PLOT TITLE(2 CARDS REQUIRED, MAX 60 CHAR EACH)
C**  NTITL-NO. OF CHAR ON EACH TITLE CARD

```

```

101 FORMAT(60A1,8X,I2)
      CALL PLOT2(NX(ITYPE),NXL(ITYPE),INCX(ITYPE),TX(ITYPE)

```


MAINLINE GCPLT

... (CONT'D)

```

*,TITLE,NTITL
1,INCXL(ITYPE))
  READ(5,106) YBASE,BMV

```

```

C** YBASE-BASELINE IN DIGITAL UNITS (0-16383)
C** BMV-BASELINE IN M.V.

```

```

YMAX=19.-BMV
  READ(5,100) NPKS

```

```

C** NPKS-NUMBER OF SEPARATE PLOTS PER CHROMATOGRAM

```

```

  CALL FPLOT(-2,0.,BMV)
  DO 40 I=1,NPKS
    READ(5,106) XSTRT,XEND,PSTRT,AMP

```

```

C** XSTRT-STARTING RECORD NO.
C** XEND-FINAL RECORD NO.
C** PSTRT-POSITION ON PLOT OF XSTRT (IN SEC.)
C** AMP-AMPLIFICATION FACTOR FOR PLOTTING SMALL PEAKS

```

```

  READ(5,100) INCR

```

```

C** INCR-INCREMENT OF DATA TO BE PLOTTED(I.E. 2 MEANS EVERY
C** IOTHER POINT

```

```

  ADDX=INCR/16.
  IXS=XSTRT
  IXE=XEND
  X=PSTRT
  CALL FPLOT(0,X,BMV)
  NFIL=IXS-2*INCR
  READ(100,NFIL) IY(1)
  NFIL=IXS-INCR
  READ(100,NFIL) IY(2)
  DO 40 NFIL=IXS,IXE,INCR
    READ(100,NFIL) IY(3)
    Y=((IY(2)-YBASE)/16383.*20.)*AMP+BMV
    IF(Y-BMV)30,31,31
30 Y=BMV
31 IF(Y-YMAX)35,35,34
34 Y=YMAX

```


MAINLINE GCPLT

... (CONT'D)

```

35 IY(1)=IY(2)
   IY(2)=IY(3)
   X=X+ADDX
40 CALL FPLOT(0,X,Y)
106 FORMAT(5F10.5)
   CALL FPLOT(0,X,BMV)
   CALL FPLOT(-1, TX(ITYPE), BMV)
   READ(5,100) NLABL

```

C** NLABL-NO. OF SUBTITLES FOR PLOT

```

   IF(NLABL)70,70,32
32 DO 33 I=1,NLABL
   READ(5,101) LAB,N

```

C** LAB-SUBTITLE

C** N-NO. OF CHARACTERS IN SUBTITLE

```

   READ(5,106)X,Y,XS,YS,THT

```

C** X,Y-POSITION OF THE SUBTITLE(SEC. AND M.V.)

C** XS,YS-SIZE OF LETTERS(IN.)

C** THT-ANGLE OF LETTERS IN RADIANS

```

   CALL FCHAR(X,Y,XS,YS,THT)
33 WRITE(7,107)(LAB(J),J=1,N)
107 FORMAT(60A1)
70 CALL FPLOT(0, TX(ITYPE), 0.)
   CALL SCALF(1.,1.,0.,0.)
   CALL FPLOT(0,2.,-2.5)
   GO TO 1
80 CALL EXIT
   END

```


SUBROUTINE PLOT2

SUBROUTINE PLOT2

```

C      ****
C      *
C      *
C      *  AXIS GENERATION, ANNOTATION AND PLOT SCALING.
C      *
C      ****

```

```

SUBROUTINE PLOT2(NX,NXL,INCX,TX,TITLE,NTITL,INCXL)
REAL LABX(3),LABY(4)
INTEGER TITLE(2,60)
DIMENSION XLAB(60),NTITL(2)
DATA LABX/'TIME',' (MI','N.) '/,LABY/'SIGN','AL ('
*, 'M.V.','') '/'
NY=20
NYL=10
XSPC=2.1
YSPC=2.5
DO 9 I=1,60
9 XLAB(I)=I-1.
CALL FPLLOT(-2,.5,.5)
CALL POINT(0)
CALL FPLLOT(1,XSPC,YSPC)
DISTX=8.4/NX
DISTY=5.0/NY
CALL SCALF(1.,1.,0.,0.)
DXL=INCXL*DISTX
DYL=5.0/NYL
NXL=NXL+1
CALL FGRID(0,0.,0.,DISTX,NX)
CALL FGRID(1,8.4,0.,DISTY,NY)
CALL FGRID(2,8.4,5.0,DISTX,NX)
CALL FGRID(3,0.,5.0,DISTY,NY)
XN=-.15
YN=-.25
DO 20 I=1,NXL,INCX
CALL FCHAR(XN,YN,.10,.15,0.)
WRITE(7,100) XLAB(I)
20 XN=XN+DXL
NXL=NXL-1
100 FORMAT(F4.1)
XN=(8.4-1.65)/2.
YN=-.45
CALL FCHAR(XN,YN,.15,.15,0.)

```


SUBROUTINE PLOT2

...(CONT'D)

```
      WRITE(7,101) LABX
101  FORMAT(4A4)
      YN=-.85
      DO 23 I=1,2
        IF(NTITL(I))23,23,22
22    XN=(8.4-NTITL(I)*.15)/2.
        CALL FCHAR(XN,YN,.15,.15,0.)
        N=NTITL(I)
        WRITE(7,103) (TITLE(I,J),J=1,N)
23    YN=YN-.2
103  FORMAT(60A1)
      XN=-.3
      YN=0.
      DO 21 I=2,22,2
        J=I-2
        CALL FCHAR(XN,YN,.10,.15,0.)
        WRITE(7,104) J
104  FORMAT(I2)
21    YN=YN+DYL
        YN=(5.0-1.95)/2.
        XN=-.4
        CALL FCHAR(XN,YN,.15,.15,1.571)
        WRITE(7,101) LABY
        CALL FPLOT(0,0.,0.)
        UX=8.4/TX
        UY=5./20.
        CALL SCALF(UX,UY,0.,0.)
      RETURN
      END
```


MAINLINE DATPT

MAINLINE DATPT

```

C      *****
C      *
C      *
C      *   PLOTTING OF POINTS FROM G.C. FILE. THE FOLLOWING *
C      *   PLOTS ARE AVAILABLE.                             *
C      *       1. RAW SIGNAL                                 *
C      *       2. FIRST DERIVATIVE                          *
C      *       3. SECOND DERIVATIVE                         *
C      *
C      *****

```

C** PLOTS

C** VALUES FOR IDEC

	PLOT	OVERPLOT
C FIRST DERIVATIVE	1	4
C SECOND DERIVATIVE	2	5
C RAW SIGNAL	3	6

C** FUNCTIONS

```

C EXIT 0
C SPACE FOR NEW PLOT 7

```

```

DEFINE FILE 100(9600,1,U,NEXR)
INTEGER Y(13),X,DYDX1,OFFST,DLAS1,DLAS2,TITLE(2,60)
DIMENSION NTITL(2)

```

```

C** ID-PLOT DEVICE(0-PLOTTER, 1-SCOPE)
C** JSCAN-MAX. TIME ALONG X AXIS=(8/2**JSCAN) MIN.
C** DASHED LINE PARAMETER(NO. OF MOVES PER DASH)
C** NOTE..IMOV=0-SOLID LINE
C** YMAX-MAXIMUM VALUE OF PLOT VARIABLE
C** ISCAN,IEXP1,IEXP2-SCAN PARAMETERS
C** ISTRT,IEND-FILE LOCATION OF DATA(16*TIME(SEC.))
C** OFFST-OFFSET IN TIME COORDINATE(IN FILE LOCATION UNITS)

```


MAINLINE DATPT

... (CONT'D)

```

C** IY-OFFSET IN Y COORDINATE
C** IEXP0-RAW SIGNAL EXP FILTER FACTOR
C** IFILT-FILTER FLAG
C      0-NO FILTER
C      1-SPIKE FILTER
C      2-13 PT 3 RD ORDER
C      3-13 PT 5 TH ORDER
C      4-EXP
C      5-13 PT 3 RD ORDER+SPIKE
C      6-13 PT 5 TH ORDER+SPIKE
C      7-EXP+SPIKE

```

```

6 READ(5,101) IDEC
  IF(IDEC)25,25,4
4 IF(IDEC-6)7,7,24

```

```

C** READ PARAMETERS

```

```

7 READ(5,101) ID,JSCAN,IMOV,ITIT
  IF(IMOV)40,40,41
40 IMOV=32767
41 IACT=1
  IF(ITIT)53,53,52
53 NTITL(1)=0
  GO TO 54
52 DO 2 I=1,2
  2 READ(5,102)(TITLE(I,J),J=1,60),NTITL(I)
102 FORMAT(60A1,8X,I2)
54 NMOV=0
  READ(5,100) YMAX
  READ(5,101) ISCAN,IEXP1,IEXP2,ISTRT,IEND,OFFST,IY
  *,IFILT,IEXP0

```

```

C** INITIALIZE VARIABLES

```

```

  ALPHA=IEXP0/100.
  ALPH1=IEXP1/100.
  ALPH2=IEXP2/100.
  INC=2**ISCAN
  DLAS1=0
  DLAS2=0

```

```

  IF(IDEC-3)14,14,16

```

```

C** IDEC=4,5,6-OVERPLOT

```


MAINLINE DATPT

...(CONT'D)

```
16 IDEC=IDEC-3 -|
   GO TO 18
```

C** SET UP AND POSITION DESIRED DEVICE

```
14 IF(ID)11,11,10
10 CALL PLOTD(ID)
   CALL ERASE
   CALL ORGSC(0.,0.)
11 CALL FPLOT(0,3.0,2.5)
   CALL SCALF(1.,1.,2.5,2.5)
```

C** VALUE OF YMIN DEPENDS ON TYPE OF PLOT

```
   IF(IDEC-3)5,8,5
8  YMIN=0.
   GO TO 17
5  YMIN=-YMAX
```

C** CONSTRUCT AXIS

```
17 CALL AXIS(YMAX,JSCAN,IDEC,YMIN,TITLE,NTITL)
```

C** READ INITIAL POINTS TO START 13 POINT STRING

```
18 NFIL=ISTRT-7*INC
   DO 12 I=1,12
   NFIL=NFIL+INC
12 READ(100'NFIL) Y(I)
```

C** PLOT

```
   X=OFFST
   READ(100'NFIL) Y(13)
```

C** SUBROUTINE FILTR PERFORMS DESIRED FILTERING ON RAW
C** SSIGNAL

```
   CALL FILTR(Y,IFILT,ALPHA)
```

C** DER CALCULATES THE FIRST OR SECOND DERIVATIVE

```
   CALL DER(Y,DYDX1,ALPH1,ALPH2,IDEC,DLAS1,DLAS2)
   RX=X
```


MAINLINE DATPT

... (CONT'D)

RDYDX=DYDX1+IY

C** NOTE..IF PLOTTING RAW SIGNAL RDYDX=Y(7)

```

      CALL FPLOT(-2,RX,RDYDX)
      CALL SHUFF(Y)
      I1=ISTR+INC
      DO 13 I=I1,IEND,INC
      X=X+INC
      NFIL=I+6*INC
      READ(100,NFIL) Y(13)
      CALL FILTR(Y,IFILT,ALPHA)
      CALL DER(Y,DYDX1,ALPH1,ALPH2,IDEC,DLAS1,DLAS2)
      RX=X
      RDYDX=DYDX1+IY
      CALL FPLOT(0,RX,RDYDX)
      NMOV=NMOV+INC
      IF(IMOV-NMOV)42,42,13
42    CALL FPLOT(IACT,RX,RDYDX)
      NMOV=0
      GO TO(43,44),IACT
43    IACT=2
      GO TO 13
44    IACT=1
13    CALL SHUFF(Y)
      CALL FPLOT(1,XMIN,YMIN)
      GO TO 6

```

C** SPACE FOR END OF PLOT

```

24    CALL SCALF(1.,1.,2.5,2.5)
      CALL FPLOT(0,9.,0.)
      CALL SCALF(1.,1.,0.,0.)
      GO TO 6
25    CALL EXIT
100   FORMAT(2F10.5)
101   FORMAT(10I5)
      END

```


SUBROUTINE AXIS

SUBROUTINE AXIS

```

C      ****
C      *
C      *
C      *   AXIS GENERATION, ANNOTATION AND PLOT SCALING.
C      *
C      ****

```

```

SUBROUTINE AXIS(YMAX,JSCAN,IDEC,YMIN,TITLE,NTITL)
INTEGER TITLE(2,60)
DIMENSION NTITL(2)
Y1=2.5
Y2=6.
Y3=9.5
YL=7.
NY=10
NX=6
XMIN=0.
XMAX=30.*16.*16./2**JSCAN
SY=YL/NY
SX=5.0/NX
CALL FGRID(1,2.5,Y1,SY,NY)
CALL FGRID(0,2.5,Y3,SX,NX)
CALL FGRID(3,7.5,Y3,SY,NY)
CALL FGRID(2,7.5,Y1,SX,NX)
IF(IDEC-3)2,3,2
2 CALL FGRID(0,2.5,Y2,SX,NX)
3 INC=XMAX/(NX*16)
NX=NX-1
IX=0
XS=2.4
YS=Y1-.2
DO 10 I=1,NX
IX=IX+INC
XS=XS+SX
CALL FCHAR(XS,YS,.1,.15,0.)
10 WRITE(7,100) IX
100 FORMAT(I3)
IDIV=2
INC=(YMAX/NY-YMIN/NY)*IDIV
SY=IDIV*SY
IY=YMIN
XS=1.8
YS=Y1-SY
NY=NY+1
DO 20 I=1,NY,IDIV
YS=YS+SY

```


SUBROUTINE AXIS

...(CONT'D)

```
      CALL FCHAR(XS,YS,.1,.15,0.)
      WRITE(7,101) IY
20    IY=IY+INC
101  FORMAT(I6)
      XS=1.7
      YS=Y2-.8
      CALL FCHAR(XS,YS,.1,.15,1.571)
      GO TO(30,31,33),IDEC
30    WRITE(7,102)
102  FORMAT('FIRST DERIVATIVE')
      GO TO 32
31    WRITE(7,103)
103  FORMAT('SECOND DERIVATIVE')
      GO TO 32
33    WRITE(7,105)
105  FORMAT(' DIGITAL SIGNAL ')
32    YS=Y1-.4
      XS=4.5
      CALL FCHAR(XS,YS,.1,.15,0.)
      WRITE(7,104)
104  FORMAT('TIME(SEC)')
      IF(NTITL(1))21,21,40
40    NN=NTITL(1)
      XS=2.5+(5.0-NN*.1)/2.
      CALL FCHAR(XS,1.5,.1,.15,0.)
      WRITE(7,200)(TITLE(1,J),J=1,NN)
      NN=NTITL(2)
      XS=2.5+(5.0-NN*.1)/2.
      CALL FCHAR(XS,1.1,.1,.15,0.)
      WRITE(7,200)(TITLE(2,J),J=1,NN)
200  FORMAT(60A1)
21    CALL FPLOTT(0,2.5,2.5)
      UX=5./(XMAX-XMIN)
      UY=(Y3-Y1)/(YMAX-YMIN)
      CALL SCALF(UX,UY,0.,YMIN)
      RETURN
      END
```


SUBROUTINE FILTER

SUBROUTINE FILTER

```

C *****
C *
C *
C *   RAW SIGNAL FILTERING.
C *
C *****

```

```

SUBROUTINE FILTR(Y,IFILT,ALPHA)
INTEGER Y(13)
DIMENSION A3(7),A5(7)
DATA A3/-11.,0.,9.,16.,21.,24.,12.5/,B3/143./
DATA A5/110.,-198.,-160.,110.,390.,600.,338.5/,B5
*/2431./
ISAVE=IFILT
7 IF(IFILT)9,9,8
8 GO TO(1,2,3,4,1,1,1),IFILT

```

C** SPIKE FILTER

```

1 IF(Y(12)-Y(13))30,50,20
20 IF(Y(12)-Y(11))50,50,40
30 IF(Y(12)-Y(11))40,50,50
40 Y(12)=(Y(11)+Y(13))/2
50 IFILT=IFILT-3
GO TO 7

```

C** 13 PT 3 RD ORDER

```

2 SUM=0.
DO 60 I=1,7
J=14-I
60 SUM=A3(I)*(Y(I)+Y(J))+SUM
Y(7)=SUM/B3
GO TO 9

```

C** 13 PT 5 TH ORDER FILTER

```

3 SUM=0.
DO 70 I=1,7
J=14-I
70 SUM=A5(I)*(Y(I)+Y(J))+SUM
Y(7)=SUM/B5
GO TO 9

```


SUBROUTINE FILTER

...(CONT'D)

C** EXPONENTIAL FILTER

4 Y7=ALPHA*Y(7)+(1.-ALPHA)*Y(6)
Y(7)=Y7

9 IFILT=ISAVE
RETURN
END

SUBROUTINE DER

SUBROUTINE DER

```

C      ****
C      *
C      *
C      *   CALCULATION OF DESIRED DERIVATIVE.
C      *   J=1   FIRST DERIVATIVE
C      *   J=2   SECOND DERIVATIVE
C      *   J=3   RAW SIGNAL
C      *
C      ****

```

```

      SUBROUTINE DER(Y,DYDX1,ALPH1,ALPH2,J,DLAS1,DLAS2)
      INTEGER Y(13),DYDX1,DLAS1,DLAS2
      GO TO(10,20,25),J
10  DYDX1=(Y(10)-Y(4)+Y(9)-Y(5))*2
      DYDX1=DYDX1+Y(10)-Y(4)+Y(8)-Y(6)

```

C** EXPONENTIAL FILTER

```

      D=ALPH1*DYDX1+(1.-ALPH1)*DLAS1
      DYDX1=D
      DLAS1=DYDX1
      GO TO 30
20  DYDX1=(Y(13)+Y(1)-2*Y(7)+Y(12)-Y(6)+Y(2)-Y(8))*2
      DYDX1=DYDX1+Y(13)+Y(1)-2*Y(7)
      DYDX1=DYDX1+Y(3)-Y(5)-Y(9)+Y(11)

```

C** EXPONENTIAL FILTER

```

      D=ALPH2*DYDX1+(1.-ALPH2)*DLAS2
      DYDX1=D
      DLAS2=DYDX1
      GO TO 30
25  DYDX1=Y(7)
30  CONTINUE
      RETURN
      END

```


SUBROUTINE SHUFF

SUBROUTINE SHUFF

```
SUBROUTINE SHUFF(Y)
  INTEGER Y(13)
  DO 10 I=1,12
10 Y(I)=Y(I+1)
  RETURN
  END
```


B30013